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Über die Turbulenz in der Sonnenatmosphäre.

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Zusammenfassung.

Unter der Annahme, dass sich das Turbulenzelement während seiner Bewegung adiabatisch ändert, hat der Verfasser die Turbulenz in der Sonnenatmosphäre untersucht. Erstens wird die Gültigkeit des *Richardson*schen Ausdruckes für die Produktivität der Wirbel, der für die Erdatmosphäre aufgestellt ist, für die Sonnenatmosphäre verifiziert. Zweitens sind die numerischen Betrachtungen über die wirbelerzeugende und die wirbelkonsumierende Zone gemacht, und unter der Annahme der Proportionalität des Austausches zu einer Potenz der Turbulenzenergie ist die *Rossby*sche Differentialgleichung gelöst worden. Als Ergebnisse der Berechnungen ist es gefunden worden, dass sich eine turbulente Zone in der Sonnenatmosphäre befindet, deren Dicke ungefähr 7000 km beträgt, deren obere Grenze in der Chromosphäre liegt, und dass die mittlere Geschwindigkeit der turbulenten Bewegungen von der Grössenordnung von 10 km/sec ist.

Neuerdings ist von manchen Astronomen die Ansicht geäussert, dass die turbulenten Bewegungen nicht nur in der Atmosphäre, sondern auch im Innern der Sterne stattfinden. Wenn das der Fall ist, so spielt die Turbulenz astrophysikalisch eine grössere Rolle als die Molekularbewegung, sodass man ihre Einwirkung in bezug auf den inneren Aufbau und den Atmosphären-Aufbau berücksichtigen muss[1]. Nach den theoretischen Untersuchungen in den letzten Jahren ist es einerseits bekannt, dass das Strahlungsgleichgewicht nicht der einzig mögliche Zustand im Sterninnern ist, dass unter Umständen, z. B. bei der starken Zentralkonzentration der Energieerzeugung, das Strahlungsgleichgewicht labil ist und die Konvektionsströme von dauerndem Bestand sind. In der Tat wird in diesem Falle der Energietransport durch Turbulenz viel grösser als der durch Lichtquanten, infolgedessen besteht hier das konvektive Gleichgewicht an Stelle des Strahlungsgleichgewichtes. Über die Möglichkeit des Auftritts der Konvektionsströme hat H. Siedentopf[2] eingehende Untersuchungen gemacht, und L. Biermann[3] hat einige rechnerische Beispiele hierfür gegeben. Andererseits sind die Erscheinungen von Granulationen und Protuberanzen usw. in

1. Vgl. S. Rosseland. M. N. **89** (1929) 49. 2. H. Siedentopf, A. N. **244** (1932) 273; **249** (1933) 33. 3. L. Biermann, Z. f. Ap. **5** (1932) 117.

der Sonnenoberfläche eine Beobachtungstatsache, welche darauf hindeutet, dass die Turbulenz in Wirklichkeit dort stattfindet. Ausserdem sind die turbulenten Bewegungen in der Chromosphäre nach den spektroskopischen Untersuchungen[1] bestätigt worden. Insgesamt ist es heute keineswegs zu bezweifeln, dass die Turbulenz mehr oder weniger in den Himmelskörpern in Erscheinung tritt.

In 1930 zeigte A. Unsöld[2], dass der Ionisationsvorgang auf einem etwa von $\tau = 2$ bis $\tau = 30$ in optischen Tiefen liegenden Gebiete eine sogenannte „Konvektionszone" zur Folge hat, und er schlug vor, die in der Sonnenatmosphäre zu beobachtenden turbulenten Bewegungen auf eine solche Zone zurückzuführen. Es scheint also für die Untersuchungen der Sonnenatmosphäre interessant zu sein, den Betrag und die Verteilung der in solcher Zone erzeugten Turbulenzen etwas eingehend zu betrachten[3]. Da man aber im gegenwärtigen Stande unseres Wissens keine sichere Kunde über die Eigenschaften der Turbulenz in Himmelskörpern hat, ist es sehr schwer, eine genaue Lösung dieses Problemes zu erhalten. Es soll in dieser Abhandlung nach der Methode von C. G. Rossby[4] näherungsweise gelöst werden.

§ 1. Der Wirbel lässt sich als eine Wärmemaschine ansehen, welche nützliche Wärme in kinetische Energie verwandelt. L. F. Richardson[5] hat bei trockener Luft einen Ausdruck für diese Verwandlung pro Volumeneinheit pro Zeiteinheit abgeleitet, nämlich;

$$C_H \frac{g}{T} \left\{ \left(\frac{dT}{dz} \right)_{ad} - \frac{dT}{dz} \right\}, \qquad \text{.....(1)}$$

worin g die Gravitationsbeschleunigung, T die Temperatur, C_H der Austausch (die sogenannte Wirbelkonvektivität), und $\left(\frac{dT}{dz} \right)_{ad}$ der adiabatische Temperaturgradient ist. Er hat dabei von einer als „potentielle Temperatur" zu bezeichnenden Grösse, θ, Gebrauch gemacht, deren Gesamtmenge in einem bestimmten Teil der Luft immer erhalten wird, ganz unabhängig von jeder Massenvertauschung innerhalb desselben. Unter θ kann man diejenige Temperatur verstehen, die die

1. W. H. McCrea, M. N. **89** (1929) 718.
2. A. Unsöld, Z. f. Ap. **1** (1930) 139; **2** (1931) 209.
   Vgl. auch, H. Siedentopf, A. N. **245** (1932) 85; **247** (1933) 297. R. Wildt, Z. f. Ap. **9** (1934) 176.
3. Vgl. S. Chandrasekhar, M. N. **94** (1934) 14, 726. W. H. McCrea, M. N. **95** (1934) 80.
4. C. G. Rossby, Mo. Wea. Rev. **54** (1926) 321.
5. L. F. Richardson. Proc. R. S. L. A, **96** (1920) 9; **97** (1920) 355.

Masse der Luft zeigen würde, wenn sie adiabatisch unter einen normalen Druck p_s gebracht würde, nämlich, $\theta = T(p/p_s)^{-n}$, wo $n = 1 - \frac{1}{\gamma}$ und $\gamma = \frac{C_p}{C_v}$ das Verhältnis der spezifischen Wärmen bedeutet. Da der adiabatische Temperaturgradient, wegen der konstanten spezifischen Wärmen der Luft und des Gasgesetzes, eine eigentümliche Konstante bei der Erdatmosphäre ist, wird die Turbulenz durch Konvektion sobald dann verursacht, wenn der wahre Temperaturgradient unter Einfluss der Sonnen- oder Erdoberflächenstrahlung u. a. so vergrössert wird, dass der Ausdruck (1) positiv wird, d. h. $\left|\frac{dT}{dz}\right| > \left|\left(\frac{dT}{dz}\right)_{ad}\right|$. In der Sonnenatmosphäre ist die Sache etwas anders. Der wahre Temperaturgradient lässt sich durch Strahlungsgleichgewicht bestimmen, denn die Strömung der Strahlungsenergie ist dort überwiegend grösser als die der Energietransporte aller anderen möglichen Art[1]. Die turbulenten Bewegungen werden jedoch durch Konvektion verursacht, falls der adiabatische Temperaturgradient kleiner als der wahre Temperaturgradient wird, indem jede Schwankung in kritischen Ionisationszuständen die Werte der spezifischen Wärmen stark beeinflusst.

Aber wir können nicht dabei eine so bequeme Quantität, wie *Richardsons* θ, definieren, sodass man nicht (1) ohne weiteres auf unseren Fall anwenden darf. Wenn man aber diesen Ausdruck mit Hilfe der spezifischen Entropie S in

$$C_H\left(\frac{dT}{dz}\right)_{ad}\frac{dS}{dz} \qquad (1')$$

umformt, so besitzt diese Grösse eine allgemeinere Gültigkeit als (1), denn (1′) enthält nur die thermodynamischen Quantitäten, vom Austausch C_H abgesehen, befreit von den hydrostatischen Bedingungen. Es liegt also nahe, annehmen zu dürfen, dass (1′) auch in unserem Falle gilt. Das soll im folgenden nach thermodynamischen Betrachtungen der Konvektionsvorgänge bewiesen werden.

Es werde angenommen, dass *das Turbulenzelement während seiner Bewegung immer die adiabatische Bedingung erfüllt* und man den Strahlungsdruck vernachlässigen kann. Nun fassen wir in der Sonnenatmosphäre zwei horizontale Schichten L_1, L_2 ins Auge, deren vertikale Entfernung l ist. Es seien T_1, T_2; p_1, p_2; S_1, S_2 beziehungsweise die mittleren Temperaturen, die Gasdrucke und die spezifischen Entropien je in L_1, L_2. Die in der Zeiteinheit von L_1 zu L_2 durch Turbulenz zu

1. Vgl. H. Siedentop f. A. N. **247** (1933) 304.

übertragende Gasmasse muss der entsprechenden Gasmasse in der entgegengesetzten Richtung gleich sein. Wir bezeichnen deise Masse mit m und wollen uns einen thermodynamischen Zyklus denken, welcher besteht in :— 1. Die Masse m stehe zunächst in einem Zustande (T_1, p_1, S_1) ; sie dehne sich durch Übergang $L_1 \rightarrow L_2$ adiabatisch aus, und p_1, T_1 werden p_2, T_1'. 2. Vom Zustande (T_1', p_2, S_1) werde sie durch Mischung unter konstantem Druck p_2 in den der Schicht L_2 eigentümlichen Zustand (T_2, p_2, S_2) gebracht. 3. Vom Zustande (T_2, p_2, S_2) werde eine Gasmenge von derselben Masse m adiabatisch durch Übertragen von L_2 zu L_1 in den Druck p_1 zusammengedrückt, dabei werde ihre Temperatur T_2'. 4. Schliesslich werde sie durch Mischung unter konstantem Druck p_1 in den Anfangszustand (T_1, p_1, S_1) gebracht. Dann lässt sich die während dieses Zyklus von aussen zugeführte Wärmemenge durch den Flächeninhalt im Entropie-Temperatur-Diagramm, $\int T dS$, geben. Daher folgt sogleich für die Gesamtzunahme pro Zeiteinheit der turbulenten Energie in hinreichend grossem Volumen V der Ausdruck :

$$\sum m(T_1' - T_1)(S_2 - S_1) = \sum m l^2 \left(\frac{dT}{dz}\right)_{ad} \frac{dS}{dz}, \qquad \ldots\ldots\ldots(2)$$

bis auf die kleinen Glieder von höherer Ordnung, wobei sich die Summe auf die Paare der gegeneinander die Masse austauschenden Schichten in V bezieht. Bezeichnet man mit C_H den räumlichen Mittelwert von $\sum m l^2$, so erhält man schliesslich aus (2), als die Zunahme der turbulenten Energie pro Zeiteinheit pro Einheitsvolumen, $C_H \left(\frac{dT}{dz}\right)_{ad} \frac{dS}{dz}$, was nichts anderes als der *Richardson*sche Ausdruck in Form (1′) ist.

§ 2. Im vorhergehenden Paragraphen haben wir bewiesen, dass der *Richardson*sche Ausdruck auch in der Sonnenatmosphäre zu brauchen ist. Jetzt ist man imstande, die *Rossby*sche[1] Differentialgleichung für die Energie der Turbulenz auf die Sonnenatmosphäre anzuwenden. Die Gleichung lautet bei dem stationären Zustand :

$$C_M \Gamma + C_H \left(\frac{dT}{dz}\right)_{ad} \frac{dS}{dz} + \frac{d}{dz}\left(C_E \frac{dE}{dz}\right) - f\rho E = 0, \qquad (3)$$

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1. C. G. Rossby. loc. cit. 2. Bei nicht-stationärem Zustande wird noch allgemeiner $\rho \frac{DE}{Dt}$ auf der rechten Seite, und $p_t \frac{D\rho}{\rho Dt}$ auf der linken Seite eintreten, und die allgemeine Energiegleichung wird infolgedessen von der Form $\rho \frac{D}{Dt}(E+U) = (p+p_t)\frac{D\rho}{\rho Dt} + C_M \Gamma + \frac{\partial}{\partial z}\left\{C_E \frac{\partial E}{\partial z} + C_H T \frac{\partial S}{\partial z} - H\right\}$ sein, wobei U die innere Energie des Gases, p_t der turbulente Druck und H der Strahlungsfluss ist.

worin $\Gamma=\left(\frac{\partial\bar{u}}{\partial z}\right)^2+\left(\frac{\partial\bar{v}}{\partial z}\right)^2$ und E die Turbulenzenergie pro Einheitsmasse ist. Das erste Glied der linken Seite von (3) bedeutet einen Bruchteil der kinetischen Energie der mittleren Bewegung (in (3) nur horizontale Bewegungen ($\bar{u}$, $\bar{v}$) angenommen), der in Zeit- und Volumeneinheit durch die turbulente Reibung in turbulente Energie umgewandelt wird; C_M ist hier der Koeffizient der turbulenten Reibung. Das dritte Glied lässt sich der Diffusion der Turbulenzenergie zuschreiben, nämlich der durch eine horizontale Einheitsfläche strömenden Turbulenzenergie, $-C_E\frac{dE}{dz}$: Hier ist C_E auch ein zu C_H, C_M analoger Koeffizient, aber nicht wesentlich gleich jedem von beiden. Das letzte Glied bedeutet denjenigen Bruchteil der Energie, die in Zeit- und Volumeneinheit durch die molekulare Viskosität in Wärme verwandelt wird. Für f hat Richardson den Ausdruck $f=\frac{2\nu\pi^2}{\rho\sigma^2}$ gegeben, worin ν die molekulare Viskosität, σ die lineare Dimension des Turbulenzelementes ist. Bezeichnet man mit v das spezifische Volumen, so wird das Differential der spezifischen Entropie durch

$$dS=\frac{C_p}{T}dT-\left(\frac{\partial v}{\partial T}\right)_p dp \qquad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

gegeben. Für die adiabatische Änderung ergibt sich

$$\frac{C_p}{T}\left(\frac{dT}{dz}\right)_{ad}=\left(\frac{\partial v}{\partial T}\right)_p\frac{dp}{dz}. \qquad \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Aus (3) folgt, (4) und (5) berücksichtigend,

$$C_M\Gamma+C_H\frac{R}{\mu}\frac{dp}{pdz}\left\{1-\frac{T}{\mu}\left(\frac{\partial\mu}{\partial T}\right)_p\right\}\left\{\frac{dT}{dz}-\left(\frac{dT}{dz}\right)_{ad}\right\}-f\rho E$$
$$=-\frac{d}{dz}\left(C_E\frac{dE}{dz}\right), \qquad \ldots\ldots\ldots\ldots\ldots\ldots(6)$$

worin μ das mittlere Molekulargewicht bedeutet. Wir wollen nach Rossby die durch den in der linken Seite dieser Gleichung stehenden Ausdruck gegebene Grösse „Wirbelproduktivität" nennen[1].

§ 3. Wir wollen nunmehr die in den vorhergehenden Paragraphen ermittelten Formeln auf die Sonnenatmosphäre sowie die unmittelbar darunter liegenden Schichten anwenden, angenommen, dass sie sich im mechanisch-thermodynamischen Gleichgewicht befinden. Die Temperaturverteilung wird dabei, wie in §. 1 erwähnt, in erster Annäherung

1. Bei Rossby soll man unter „Wirbelproduktivität" anstatt diesen Grösse ihr Verhältnis zu E verstehen.

durch das Strahlungsgleichgewicht bestimmt. Bezeichnet man mit T_0, τ, p_t die Grenztemperatur, die optische Tiefe und den turbulenten Druck, und nimmt man den Absorptionskoeffizienten k als konstant an, so ergeben sich

$$T^4 = T_0^4\left(1+\frac{3}{2}\tau\right),\quad \frac{dp}{dz} = -\beta\rho g,\quad p+p_t = \frac{g}{k}\tau,\quad \text{wo}\quad \beta \equiv \frac{dp}{dp+dp_t}. \qquad \cdots\cdots(7)$$

Da der turbulente Druck mit der Turbulenzenergie in Relation $p_t = \frac{2}{3}\rho E$ steht, folgt aus (7) sofort $\rho = \dfrac{g/k}{\frac{R}{\mu}T+\frac{2}{3}E}\tau$, und demgemäss ergibt sich als der Temperaturgradient

$$\frac{dT}{dz} = -\frac{\mu}{R}\beta' g\frac{T^4-T_0^4}{4T^4},\qquad \beta' \equiv \frac{p}{p+p_t} = \frac{\frac{R}{\mu}T}{\frac{R}{\mu}T+\frac{2}{3}E}. \qquad \cdots\cdots(8),\ (9)$$

In unserem Falle lässt sich die Gleichung (6) wegen (5), (7) und (8) umschreiben:

$$C_H\frac{\mu\beta^2 g^2}{RT}\left(1-\frac{T}{\mu}\left(\frac{\partial\mu}{\partial T}\right)_p\right)\left(\frac{\beta'}{\beta}\,\frac{T^4-T_0^4}{4T^4}-n\right)+\frac{d}{dz}\left(C_E\frac{dE}{dz}\right) = 0,[1] \qquad \cdots\cdots(10)$$

worin ist: $$n = \left(\frac{d\log T}{d\log p}\right)_{\text{adiabatisch}} = \frac{p}{C_p}\left(\frac{\partial v}{\partial T}\right)_p. \qquad \cdots\cdots(11)$$

Setzt man nun $$\frac{\mu\beta^2 g^2}{RT} \equiv \alpha^2,\quad \phi \equiv \frac{\psi}{\alpha^2} \equiv \left\{1-\frac{T}{\mu}\left(\frac{\partial\mu}{\partial T}\right)_p\right\} \times\left\{\frac{\beta'}{\beta}\,\frac{T^4-T_0^4}{4T^4}-n\right\}, \qquad \ldots(12)$$

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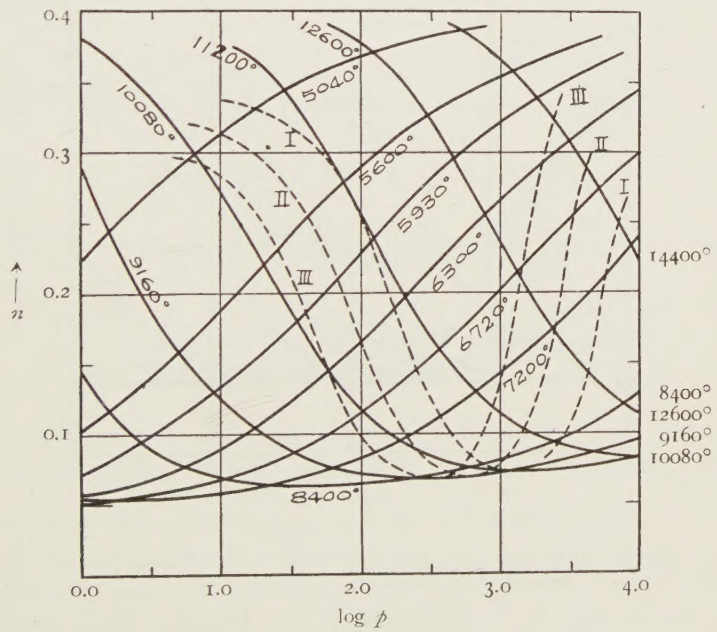
1. In der Gleichung ist die durch molekulare Viskosität zu dissipierende Turbulenzenergie vernachlässigt. Die Richtigkeit solcher Annäherung ist in folgender Weise zu verifizieren: Man vergleiche grössenordnungsmässig das Glied $f\rho E$ mit dem zweiten Gliede $C_H\left(\frac{dT}{dz}\right)_{ad}\frac{dS}{dz}$ der linken Seite von (3) oder mit (1). Mit $g \fallingdotseq 3\times10^4$, $T \approx 10^4$, $\rho \approx 10^{-8}$ und $\sigma \approx 10^7$ (was der linearen Dimension von kleiner Granulation entspricht) erhält man dann nach dem Ausdruck für f, $\dfrac{f\rho E}{C_H\left(\frac{dT}{dz}\right)_{ad}\frac{dS}{dz}} \approx \bar{v}\times10^{-8}$, dabei den *Prandtl*schen Ausdruck für den Austausch berücksichtigend, nämlich $C_H \approx \rho\bar{v}\sigma$ ($\bar{v}$ = die mittlere Geschwindigkeit der turbulenten Bewegungen). Aus der Grössenordnung 10^5 von $\bar{v}$ (vgl. §. 4), folgt dann die Richtigkeit unserer Annahme für die Sonnenatmosphäre.

so erhält man $$C_H\psi+\frac{d}{dz}\left[C_E\frac{dE}{dz}\right]=0, \qquad \ldots\ldots\ldots(13)$$

worin das erste Glied in der linken Seite die „Wirbelproduktivität" der Konvektion gibt. In einem und demselben Turbulenzelemente ändern sich freilich der Druck, die Temperatur und der Ionisationsgrad, und zwar verschieden in ihren Änderungen für verschiedene Örter, wegen der verschiedenen Bedingungen der Umgebung. Entsprechend ändern sich $n=\left(\frac{d\log T}{d\log p}\right)_{ad}$ und μ, daher auch ϕ mit der Tiefe. Wir wollen also zunächst die Werte von ϕ als Funktion der optischen Tiefe berechnen.

Wir wollen annehmen[1], dass die Sonnenatmosphäre der Einfachheit halber nur aus einem einzigen Gase, Wasserstoff, besteht. Es seien x, χ der Ionisationsgrad und das Ionisationspotential (13,54 Volt). Dann erhält man nach der *Saha*schen Formel, $\log\frac{x^2}{1-x^2}p=\frac{5}{2}\log T-\frac{\chi}{\varkappa T}+C$ worin $\varkappa$ die *Boltzmann*sche Konstante und C die chemische Konstante für das Elektron bedeutet,

Fig. 1



1. Vgl. z. B. Anm. in S. 305.

$$1-\frac{T}{\mu}\left(\frac{\partial\mu}{\partial T}\right)_p = 1+\frac{1}{2}x(1-x)\left(\frac{5}{2}+\frac{\chi}{\varkappa T}\right), \quad (14)$$

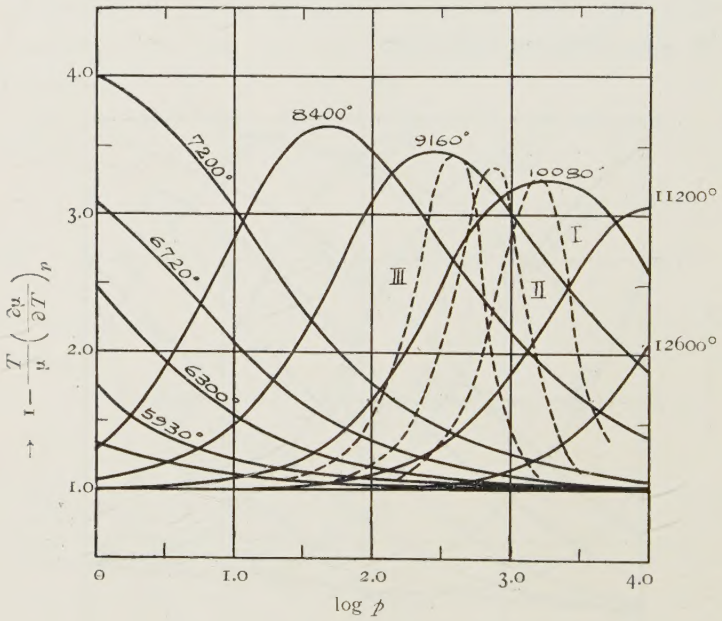
berücksichtigt, dass das mittlere Molekulargewicht umgekehrt proportional zur Gesamtzahl der unabhängigen Partikeln sein muss.

Andererseits, von dem Ausdruck für die Entropie der Mischung von neutralen Atomen, Ionen und Elektronen ausgehend, hat Unsöld[1] einen Ausruck für n abgeleitet:

$$n=\frac{2+x(1-x)\left(\frac{5}{2}+\frac{\chi}{\varkappa T}\right)}{5+x(1-x)\left(\frac{5}{2}+\frac{\chi}{\varkappa T}\right)^2}. \quad \ldots\ldots\ldots(15)$$

In Fig. 1, 2 sind n und $1-\frac{T}{\mu}\left(\frac{\partial\mu}{\partial T}\right)_p$ als Funktion von T und p veranschaulicht.

Fig. 2

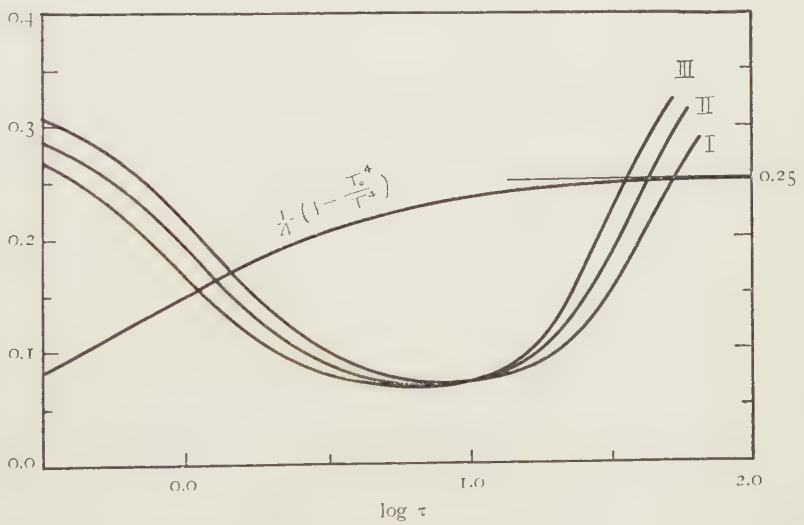


Nun ergibt sich aus (7), (9), $p=\frac{g\beta'}{k}\tau$. Mittels dieser Relation und (7) lassen sich p, T als Funktion der optischen Tiefe bestimmen,

1. A. Unsöld loc. cit.

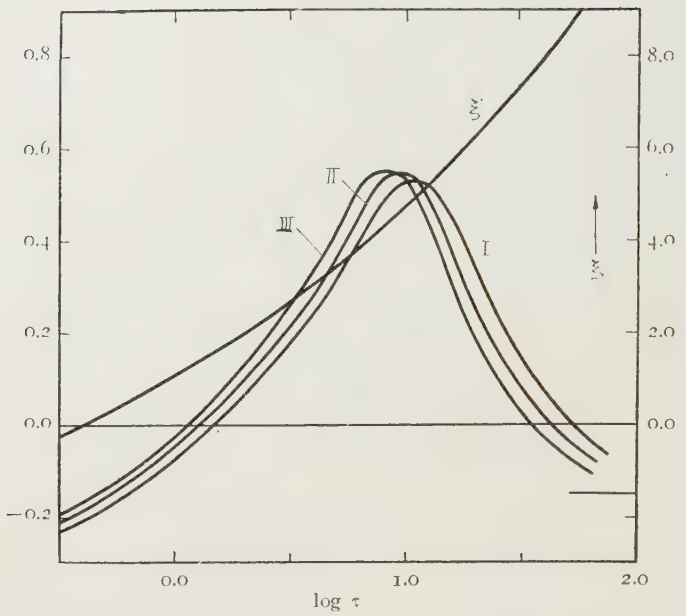
und man ist jetzt imstande, die Werte von n, $1-\frac{T}{\mu}\left(\frac{\partial\mu}{\partial T}\right)_p$ in der Sonnenatmosphäre aus Fig. 1 und 2 als Funktion von τ abzulesen. Zu diesem Zwecke hat man aber zunächst den Wert von β' zu kennen, der seinerseits erst dann errechnet werden könnte, wenn man das Problem gelöst hätte. Wir dürfen aber als einen für unser Problem geeigneten Wert von β' in erster Annäherung den mittleren Wert derselben in der *wirbelerzeugenden Zone* annehmen, weil die Wirbelproduktivität eine viel wichtigere Rolle im Probleme als die entgegengesetzte Wirkung in den beiden wirbelkonsumierenden Zonen spielt. Die gestrichenen Kurven I, II, III in Fig. 1 und 2 entsprechen den Verläufen von T, p in der Sonnenatmosphäre, respektive für $\frac{k}{\beta'}=200,\ 350,\ 600$ ($T_0=4830^\circ$ gesetzt). In Fig. 3 sind n und $\frac{1}{4}\left(1-\frac{T_0^4}{T^4}\right)$ als Funktion von

Fig. 3



τ dargestellt. Setzt man näherungsweise $\beta=\beta'$, so kann man sogleich den zweiten Faktor von ϕ aus der Abbildung abschätzen. Dabei ist zu bemerken, dass das Gebiet, wo die n-Kurve oberhalb der $\frac{1}{4}\left(1-\frac{T_0^4}{T^4}\right)$-Kurve liegt, der wirbelkonsumierenden Zone entspricht, und sonst der wirbelerzeugenden Zone. Schätzt man weiter den ersten Faktor aus Fig. 2 ab, so kann man schliesslich den Wert von ϕ als Funktion

Fig. 4



von τ berechnen. Die Ergebnisse der Berechnungen sind in Fig. 4 veranschaulicht. Der Wert von z in der wirbelerzeugenden Zone wird nach Integration von (8) gegeben durch

$$\left.\begin{aligned} &\text{Konst.} - z = \frac{RT_0}{\bar{\mu}\bar{\beta}'g}\xi \\ &\xi = \frac{4T}{T_0} + \log_e\frac{T-T_0}{T+T_0} - 2\tan^{-1}\frac{T}{T_0} \end{aligned}\right\}, \qquad \ldots(16)$$

worin $\bar{\mu}$, $\bar{\beta}'$ den mittleren Wert von μ, β' in der wirbelerzeugenden Zone bedeutet. Die Kurve von ξ ist in Fig. 4 gegeben. Wenn man mit $\Delta\xi$ die Differenz der beiden Werte von ξ, für die ϕ verschwindet, bezeichnet, so gibt $\frac{RT_0}{\bar{\mu}\bar{\beta}'g}\Delta\xi$ die lineare Dimension der wirbelerzeugenden Zone. Auf diese Weise erhalten wir folgende Ergebnisse :—

Tabelle 1.

Mittlere Temperatur	Mittelswert von $\dot{\phi}$	$\Delta\xi$
10000	0.27	7.1 für $\frac{k}{\beta_1}=200$
9700	0.27	6.8 für $\frac{k}{\beta_1}=350$
9400	0.27	6.5 für $\frac{k}{\beta_1}=600$

Wie die Tabelle zeigt, bewirken β' und k keinen wesentlichen Einfluss auf $\Delta\xi$ und die mittleren Werte von ϕ, T. Wir wollen demgemäss in folgenden Betrachtungen nur von dem Werte für $\frac{k}{\beta'}=350$ Gebrauch machen. In der unteren konsumierenden Zone, deren lineare Dimension, wie wir später sehen werden, grösser als die der erzeugenden Zone ist, setzen wir als mittleren Wert von ϕ den Grenzwert -0.15 voraus, gegen den ϕ dort sehr schnell konvergiert; in der oberen konsumierenden Zone, dagegen $\phi \fallingdotseq -0.3$, die Ionisation der anderen Metallatome als Wasserstoff auch berücksichtigend (vgl. Fig. 4). Um nun die Werte von ψ aus $\psi=\alpha^2\phi$ zu berechnen, hat man die Werte von α^2 zu kennen, deren mittlere Werte in der erzeugenden und in der unteren bzw. oberen konsumierenden Zone[1] seien jeder für sich α_0^2, α_1^2, α_2^2. Es genügt aber zu unserem Zwecke nur die Verhältnisse α_1^2/α_0^2, α_2^2/α_0^2 zu berechnen. Um diese Verhältnisse abzuschätzen, gehen wir folgendermassen vor:—Nach dem *Russell*schen Resultat[2] in bezug auf die Komposition der Sonnenatmosphäre erhält man leicht nach einer Reihe von einfachen Rechnungen $\mu=2.0$, für die obere konsumierende Zone, wo die Ionisation des Wasserstoffes zu vernachlässigen ist, $\mu=1.0$ für die untere konsumierende Zone, wo dieser Vorgang fast vollständig ist, und $\mu=1.4$ für die erzeugende Zone, wo $x=0.5$ angenommen ist. Wir nehmen weiter als die mittlere Temperatur vorläufig 20000°, 9700°, 5500° für die betreffenden Zonen an, und setzen, die späteren Resultate vornehmend, $p \approx p_t$ also $\beta'=\frac{1}{2}$ für die erzeugende Zone, $p \approx 2p_t$ also $\beta'=\frac{2}{3}$ für die obere konsumierende Zone und $\beta'=1$ für die untere konsumierende Zone, wegen ihrer hohen Temperatur. Mit diesen Werten erhält man dann aus (12), $\alpha_1^2=1.4\alpha_0^2$, $\alpha_2^2=4.5\alpha_0^2$.

§ 4. Die Koeffizienten C_H, C_E hängen wohl nicht nur von der Turbulenz, sondern auch vom mittleren Zustande des Gases ab. Wir setzen aber auch der Einfachheit halber voraus, dass sie eine Funktion nur von der Turbulenzenergie, E, sind, damit man die Differentialgleichung (13) sogleich integrieren kann. Obgleich man keine genaue Kenntnis über diese Funktionalform hat, liegt es doch nahe, dass sie sicher in dem Punkte verschwinden müssen, wo E verschwindet, und mit E monoton zunehmen müssen. Also können wir nach Rossby ihre Pro-

1. In folgenden machen wir auch bei anderen Grössen von den Suffixen 0, 1, 2 Gebrauch, um diese drei Zonen zu kennzeichnen. 2. H. N. Russell. Ap. J. **70** (1929) 11.

portionalität zu E annehmen, falls E hinreichend klein ist. In der Sonnenatmosphäre wird die Turbulenz vielleicht viel gewaltiger als in der Erdatmosphäre sein. Es mag also auch möglich sein, noch allgemeiner vorauszusetzen, dass sie zu der s-ten Potenz von E proportional seien. In solchen Fällen kann die Differentialgleichung (13) mit Hilfe einer Funktion, $\int_z^1 \frac{\zeta^s}{\sqrt{1-\zeta^{2s+1}}}d\zeta$, ganz auf dieselbe Weise wie im Falle, C_H, C_E=konst., gelöst werden. Wir wollen im folgenden beispielsweise nur den letzteren Fall genau untersuchen. Aus (13) folgt dann

$$\frac{d^2E}{dz^2}+\frac{C_H}{C_E}\psi=0, \qquad \text{.....(17)}$$

oder integriert, mit Integrationskonstanten A und B,

$$E=-\frac{C_H}{2C_E}\psi z^2+Az+B. \qquad \text{.....(18)}$$

Es ist selbstverständlich, dass E in einem gewissen Punkte in der wirbelerzeugenden Zone einen Maximumwert E_0 erreicht. Misst man von diesem Punkte die Höhe z, so ergibt sich aus (18)

$$E=-\frac{C_H}{2C_E}\psi_0 z^2+E_0 \qquad \text{für} \qquad h_2 \geqq z \geqq -h_1, \qquad (19)$$

worin h_1, h_2 die absoluten Beträge von z für die untere bzw. obere Grenze der erzeugenden Zone bedeuten. Sind $-H_1$, H_2 die Höhe der unteren bzw. oberen Grenze der ganzen durch die Turbulenz zu beherrschenden Zone, so lautet (18) für die konsumierenden Zonen:

$$\left.\begin{aligned} E&=-\frac{C_H}{2C_E}\psi_1(H_1+z)^2 \qquad \text{für} \qquad -H_1 \leqq z \leqq -h_1 \\ E&=-\frac{C_H}{2C_E}\psi_2(H_2-z)^2 \qquad \text{für} \qquad H_2 \geqq z \geqq h_2 \end{aligned}\right\}. \qquad \text{.....(20)}$$

Da die Turbulenzenergie E und ihr Gradient für $z=-h_1$, und h_2, sowohl aus (19) als auch aus (20) berechnet, dieselben Werte haben sollen, ergibt sich

$$\left.\begin{aligned} &\frac{h_1}{\sqrt{\frac{-\psi_1}{\psi_0-\psi_1}}}=\frac{h_2}{\sqrt{\frac{-\psi_2}{\psi_0-\psi_2}}}\equiv K, \qquad E_0=\frac{C_H}{2C_E}\psi_0K^2 \\ &h_1H_1=h_2H_2=K^2, \qquad\qquad 2H\equiv h_1+h_2 \end{aligned}\right\}. \qquad (21)$$

Hieraus sieht man, dass alle Höhen nicht von den Koeffizienten C_H, C_E, sondern von den Verhältnissen ψ_1/ψ_0, ψ_2/ψ_0 und der Höhe der erzeugenden Zone $2H$ abhängig sind. Das ist, es sei hier bemerkt, bei willkürlicher Wahl von s auch der Fall.

Wie schon oben erwähnt, können die Berechnungen bei den allgemeinen Fällen $s \neq 0$ auf dieselbe Weise durchgeführt werden. Die Ergebnisse der Berechnungen für $s=0, 1, 2, 3$ sind in Tabelle 2 zusammengestellt, in der $\zeta_1 = \frac{(E)_{z=-h_1}}{E_0}$, $\zeta_2 = \frac{(E)_{z=h_2}}{E_0}$ ist.

Tabelle 2.

s	ζ_1	ζ_2	h_1/H	h_2/H	H_1/H	H_2/H	H_1+H_2/H	F_0
0	0.56	0.17	0.84	1.16	1.9	1.4	3.3	0.8
1	0.83	0.55	0.79	1.21	4.3	2.4	6.7	2.0
2	0.89	0.70	0.78	1.22	6.7	3.3	10.0	3.1
3	0.92	0.78	0.78	1.22	9.2	4.3	13.5	4.3

F_0 ist die Maximalturbulenzenergie, in Einheiten von $\frac{C_H}{C_E}\phi_0 H^2$ gemessen. Für E_0 folgt also wegen (12), (16) der Ausdruck:

$$E_0 = \frac{C_H}{C_E}\phi_0 F_0 \left(\frac{\Delta\xi}{2}\right)^2 \frac{RT_0^2}{\mu T}, \qquad \ldots\ldots\ldots\ldots (22)$$

worin T die mittlere Temperatur in der erzeugenden Zone bedeutet. Da die Koeffizienten C_H und C_E von derselben Grössenordnung sind, darf man annäherungsweise $C_H/C_E = 1$ setzen. Mittels der Tabelle 2 und (22) erhält man dann:

s	0	1	2	3
$E_0 \times 10^{-11}$	3.5	8.9	14	19
$\bar{v}_{max} \times 10^{-5}$	8.4	13	17	19

Diese Tabelle zeigt, wie sich die Turbulenzenergie nach dem anzunehmenden Gesetz (s) in bezug auf den Massenaustausch ändert. Wenn man mit Rossby $s=1$ setzt, so beträgt die maximale mittlere Geschwindigkeit der Turbulenz $\bar{v}_{max}$ etwa 13 km/sec. Wenn ein grösserer Wert von s als wahrscheinlicher bei der Sonnenatmosphäre gilt, so wird $\bar{v}_{max}$ grösser als 13 km/sec. Nun mit $T=9700°$, $\mu=1.4$ ist $\frac{R}{\mu}T$ gleich 5.7×10^{11} c.g.s. für die wirbelerzeugende Zone. Andererseits erhält man, aus den Werten von ζ_1, ζ_2 in Tabelle 2, die mittlere Turbulenzenergie $\fallingdotseq 7.6 \times 10^{11}$ c.g.s., für $s=1$ und 1.2×10^{12} für $s=2$. Hieraus folgt $\beta' \fallingdotseq 0.5$ und 0.4 für $s=1$ bzw. 2, welche wir im vorhergehenden Paragraphen bei der Abschätzung von a_1^2/a_0^2, a_2^2/a_0^2 vornahmen. Mit diesen Werten von β' berechnet, kann man schliesslich sagen, dass ungefähr die Hälfte der oberhalb der betrachteten Schicht liegenden Gesamtmasse durch den Turbulenzdruck getragen wird. Alle in Tabelle 2 gegebenen Höhen sind in Einheiten

von der Halbdicke der wirbelerzeugenden Zone, nämlich $H=\frac{\Delta\xi}{2}\frac{RT_0}{\mu\bar{\beta}'g}$ ausgedrückt. Diese letztere beträgt 7.9×10^7 cm, mit $T_0=4830^\circ$, $\mu=1.4$, $\beta'=0.45$, $\Delta\xi=6.8$. Demgemäss erhält man als die Gesamtdicke der turbulenten Zone 5300, 7900 km für $s=1$ bzw. 2. Wir finden also in der Sonnenatmosphäre die Möglichkeit des Vorhandenseins einer turbulenten Zone von ziemlich grosser linearer Dimension, etwa 7000 km, deren obere Grenze wohl in der Chromosphäre[1] liegt. Es mag auch möglich sein, die beobachteten Turbulenzbewegungen in der Chromosphäre auf solche wirbelerzeugende Zone, die man üblich *Konvektionszone* nennt, zurückzuführen.

Zum Schluss ist es mir eine angenehme Pflicht, Herrn Prof. Dr. Toschima Araki für seine ständige Leitung bei der Durchführung dieser Arbeit und Herrn Prof. Dr. Tadao Namekawa für seine wertvollen Bemerkungen meinen herzlichen Dank auszusprechen.

Kyoto, Institut für Astrophysik, Juli, 1935.

1. Auf die Chromosphäre ist die Differentialgleichung (3) nicht ohne weiteres anzuwenden, denn wegen der ausserordentlich dünnen Dichte wird solche hydrodynamische Betrachtung, wie hier gemacht, nicht mehr gelten.

Transformation from Vitreous to Metallic Selenium

By **Kenzo Tanaka** and **Hshi Yu Tien** (田時雨)

(Received August 24, 1935)

Abstract

A simple relation was found between the time of annealing and the content of metallic form in the selenium specimen annealed at various temperatures near the transition point.

When vitreous selenium is heated it is changed into metallic form. In a preceding paper[1], this transformation was found by the measurement of its net density[2] to take place mainly between 68°C and 80°C for an annealing time of two hours. Further investigation was made on the relation between the time of annealing and the content of metallic form in the selenium specimen annealed at various temperatures near the transition point. The procedure of determining the weight percentage of metallic selenium contained in the specimen was the same as before. The specimens were annealed for different periods at 65°, 70°, 75° and 80°C. For every specimen the net density was measured and the weight percentage of the content of metallic form was determined.

The results are shown in Figs. 1 and 2, where experimental values are shown by dots and small circles. The time scale in Fig. 1 is five times larger than that in Fig. 2. For a certain temperature of annealing, the content of metallic part increased with the time of annealing till it reached a saturation value. The weight percentage of metallic selenium p in the specimen annealed for t hours at a certain constant temperature can be expressed in exponential form as

$$p = P(1 - e^{-c(t-t')}),$$

where P is the saturation value, c is a constant and t' is a certain time interval chosen to make the above expression fit the experimental data.

P is nearly a constant value of 78.5% for annealing temperatures between 65° and 85°. Further values of P for higher temperatures coincided with those for the time of annealing of 2 hours shown in the preceding paper. The values of c and t' for different temperatures are as is seen in the table. The value of c which determines the rate of increase in weight percent-

	65°	70°	75°	80°
c	0.062	0.089	0.495	1.11
t'	4 h	1.5 h	1.1 h	0.65 h

1. K. Tanaka: These Memoirs, **17**, 59 (1934)
2. U. Yoshida and B. Takei: These Memoirs, **15**, 1 (1932)

Fig. 1

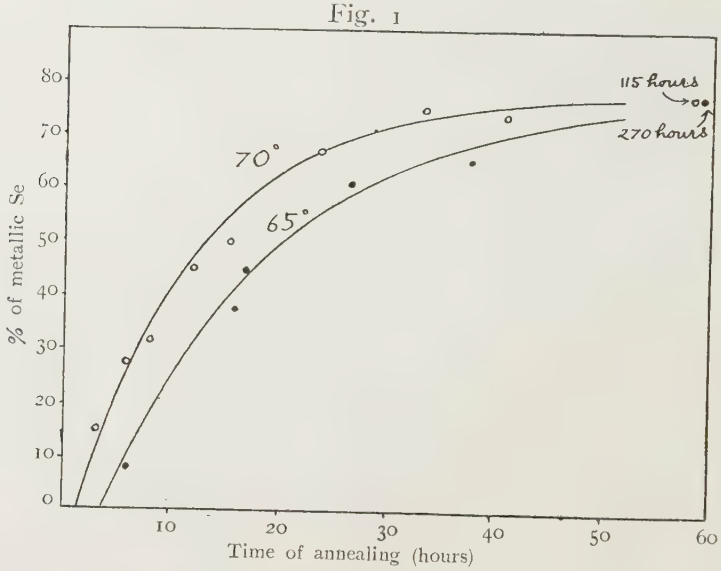
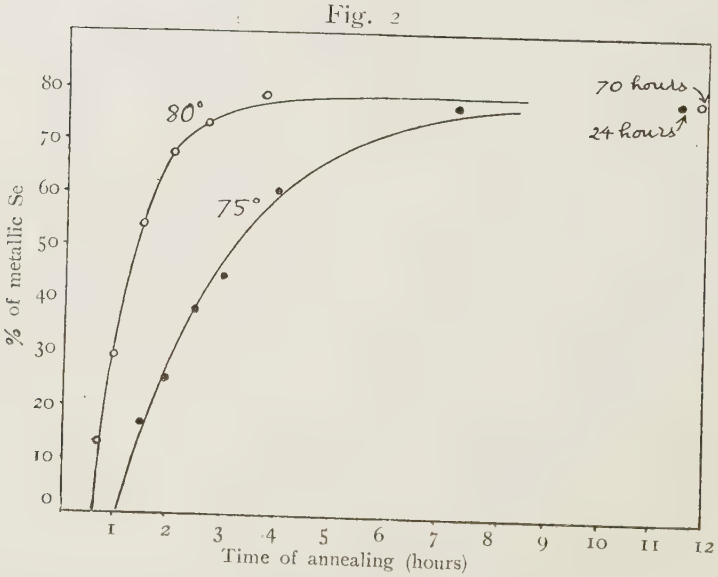


Fig. 2



age of the metallic part increases rapidly at 75° and 80°. From this it can be said that there is no definite temperature of transition from vitreous to metallic selenium; for though below 70° the rate of transition is very small, rapid transition takes place at temperatures higher than 70°.

In conclusion, the writers wish to express their sincere thanks to Prof. U. Yoshida for his kind guidance.

A Study of the Carbonization of Ramie Cellulose by means of X-Rays and the " Net Density Method "

by Chullchai Park (朴哲在)

(Received September 11. 1935)

Abstract

The carbonization of ramie cellulose at low temperatures was studied by X-rays and the " net density method "; and it was found that the perfect carbonization from cellulose to amorphous carbon occurred at about 290°C, and that no preliminary change in the lattice form of cellulose took place by heating it at lower temperatures than about 290°C before it was transformed into amorphous carbon.

Very recently, Y. Matsunaga[1], from his investigation on sugar charcoal and pitch cokes with X-rays and the " net density method ", came to the conclusion that amorphous carbon having the net density of 1,475 really exists, and that the ordinary carbon obtained by carbonizing organic substances is a mixture of this amorphous carbon (net density 1,475) and graphite (net density 2,268).

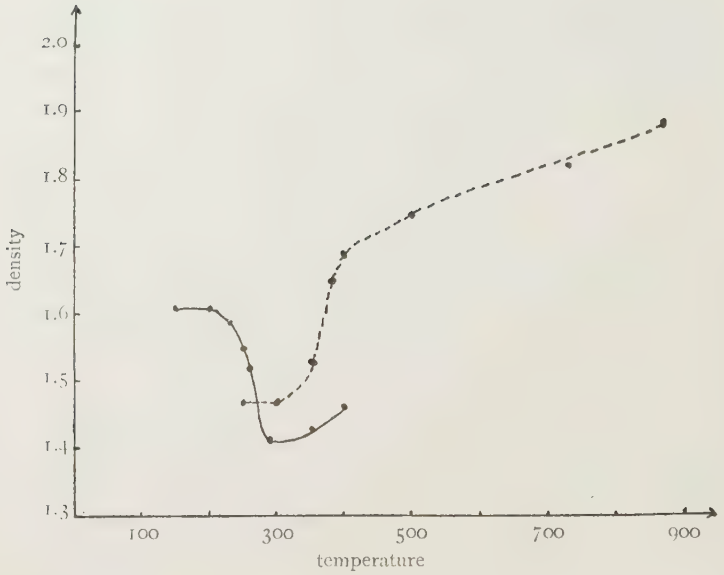
The writer first used X-rays to discover whether heating causes any preliminary change in the lattice of the crystals of ramie cellulose before it is transformed into amorphous carbon. But contrary to his expectation he failed to find any such preliminary change in the lattice form of the ramie cellulose.

The writer carbonized the sample contained in the bottom of a glass tube of about 25 cms in length and 2 cms in diameter, by heating it at various temperatures for 5 hours. The relation between the carbonizing temperature and the net density of the specimens thus obtained is shown by the curve plotted in full line in Fig. 1. As is seen from the curve in Fig. 1, the net density of the sample decreased at first with increase of the carbonizing temperature, and then increased from a temperature of about 300°C.

The sudden decrease of the net density from the value of about 1,6 at temperatures between 260°C and 280°C means that the greater part of ramie crystallites is destroyed and transformed into amorphous carbon at these temperatures. The writer also tested the samples carbonized at 260°C, 280°C and 290°C with X-rays. With the specimen carbonized at 260°C the X-ray diffraction pattern peculiar to the ramie

1. Y. Matsunaga: These Memoirs, **18**, 215 (1935).

Fig. 1



fibre appeared clearly; but with the specimen carbonized at 280°C the diffraction pattern due to the ramie fibre became very faint, and the diffraction band due to the amorphous carbon appeared prominently; and with the specimen carbonized at 290°C the diffraction pattern appearing on the photograph consisted entirely of the diffuse band peculiar to amorphous carbon, while that due to the ramie fibre could not be detected. This shows that the ramie cellulose is transformed entirely into amorphous carbon at this temperature.

Here it must be noted that the net density of the specimen was measured by the evacuation method[1] devised by Professor U. Yoshida and Mr. B. Takei.

The writer chiefly examined the net density of ramie celloluse carbonized at lower temperatures, and Y. Matsunaga studied that of sugar charcoal carbonized at higher temperatures. The results obtained by Y. Matsunaga for sugar charcoal carbonized at various temperatures for 3 hours are shown by the curve plotted in dotted line in Fig. 1. Though perfect connection between the two curves in Fig. 1 was not obtained, which would mainly be due to the difference of the original materials, yet the general tendency for the minimum net density to occur at about 290°C seems to be clearly shown by these two curves.

1. U. Yoshida and B. Takei: These Memoirs, **15**, 1 (1932).

This seems to indicate that the organic substances are transformed into amorphous carbon rather perfectly at a carbonizing temperature of about 290°C, but that at higher carbonizing temperature some of the amorphous carbon is transformed into graphite. This latter point was also tested by the writer with X-rays generated from the Cr target. With the carbon obtained by carbonizing ramie cellulose at temperatures of 600°C and 700°C, clear diffraction rings due to the graphite were detected on the background of the broad amorphous ring peculiar to amorphous carbon.

In conclusion, the writer wishes to express his sincere thanks to Professor U. Yoshida for his kind guidance, also to Lecturer, Dr. K. Tanaka and Mr. H. Tanaka for the facilities afforded to him during the present experiment.

On the Arrangement of Micro-Crystals of Silica in the Onyx

By **Masami Ichinose**

(Received September 18, 1935)

Abstract

By means of an X-ray diffraction- photograph, it has been ascertained that micro-crystals of quartz in the onyx take a fibrous arrangement, whose common axis is $[11\bar{2}0]$ and which is perpendicular to the surfaces of the banded layers in the mineral.

The onyx examined was one produced at Shiribeshi, Hokkaidô, Japan, and was semitransparent with milk-white coloured bands, as shown in Fig. 1, Plate I. From a portion of this sample where the bands are most dense and distinct, a thin plate of about 0.5 mm in thickness was cut out perpendicular to the layers of the bands, and a small pencil of X-rays, radiated from a Coolidge tube with a molybdenum target, was made to strike it in a direction perpendicular to its surface, that is, parallel to the layers of the bands. The diffraction photograph thus obtained on a photographic plate placed behind the specimen at a distance of 4 cm is reproduced in Fig. 2, Plate I. The vertical direction of this photograph is parallel to the normal to the layers of the bands.

Now the constants of a unit-cell of quartz, which belongs to the hexagonal system, are $a=4.90$ Å, $c=5.39$ Å, $\frac{c}{a}=1.10$, according to A. J. Bradley and A. H. Jay[1], and the diameters of six predominant rings in Fig. 2 coincide with the calculated values corresponding to reflecting planes $(10\bar{1}1)$, $(10\bar{1}2)$, $(20\bar{2}0)$, $(11\bar{2}2)$, $(12\bar{3}1)$, $(12\bar{3}2)$, $(20\bar{2}3)$ and $(30\bar{3}1)$ respectively, due to Mo $K\alpha$ line, as shown in the third and fourth columns of Table I. The diffraction pattern in Fig. 2 shows clearly that micro-crystals of quartz in the specimen are fibrously arranged with the common axis in the vertical direction, that is, in the direction perpendicular to the layers of the bands. And the distance between successive lattice-points along the zone axis which is assumed to be the common axis, calculated from each distance between both vertices of three pairs of layer lines except one which pass through the centre, coincide with $a=4.90$ Å, the side-length of the unit cell of

1. A. J. Bradley and A. H. Jay, Proc. Phys. Soc., **45** (1933), 507.

Table I

Planes	Specings	Diameters		Directional angles φ	
		cal.	obs.	cal.	obs.
$10\bar{1}1$	3.33 Å	17.3 mm	17.4 mm	46°31′ 90°	46°30′ 90°
$10\bar{1}2$	2.28	25.9	26.0	61°58′ 90°	61°40′ 90°
$20\bar{2}0$	2.12	28.0	27.9	28°33′ 90°	27°30′ weak
$11\bar{2}2$	1.81	33.3	33.2	41° 0′ 67°50′	41°30′ 67°50′
$12\bar{3}1$	1.54	40.2	40.1	14°41′ 49°50′ 71°12′	15°10′ 50° 0′ weak
$12\bar{3}2$	1.38	45.9		29° 8′ 54°23′ 73° 5′	
$20\bar{2}3$	1.37	46.2	46.1	54°36′ 90°	30°10′ 54°20′ weak 90°
$30\bar{3}1$	1.37	46.4		29°50′ 90°	

quartz; this means that the common axis of the fibrous arrangement is $[11\bar{2}0]$. Further, the directional angle φ of each diffraction-spot measured from the vertical line taken as the initial line with the pole at the centre, is in good agreement with the value calculated under the assumption that $[11\bar{2}0]$ is the common axis and by the employment of the formula $\cos\varphi = \cos\beta/\cos\theta$, in which β is the angle between the normal of each reflecting plane and the common axis, and θ the glancing angle to each reflecting plane. This is shown in the fifth and sixth columns of Table I, and the calculated positions of the spots are shown diagramatically in Fig. 3, which agrees well with the photograph Fig. 2. Thus the diffraction spots in Fig. 2 are fully explained.

In brief, the diffraction pattern shows that micro-crystals of quartz in the onyx take a fibrous arrangement, in which the common axis is $[11\bar{2}0]$ and is perpendicular to the banded layers in the onyx.

In conclusion, the writer expresses his deepest thanks to Prof. U. Yoshida, of Kyoto Imperial University for his kind guidance in this work.

Plate I

Fig. 1

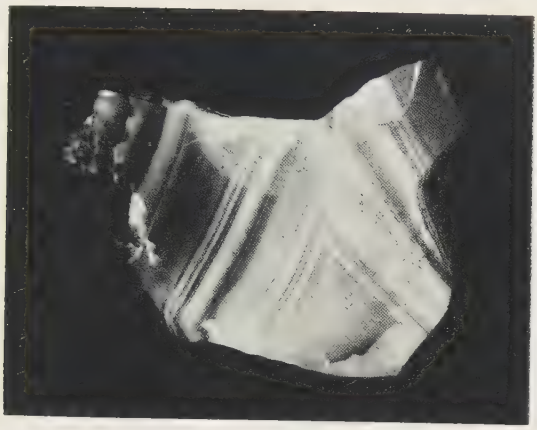


Fig. 2

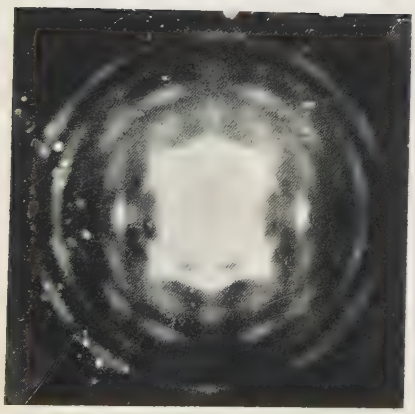
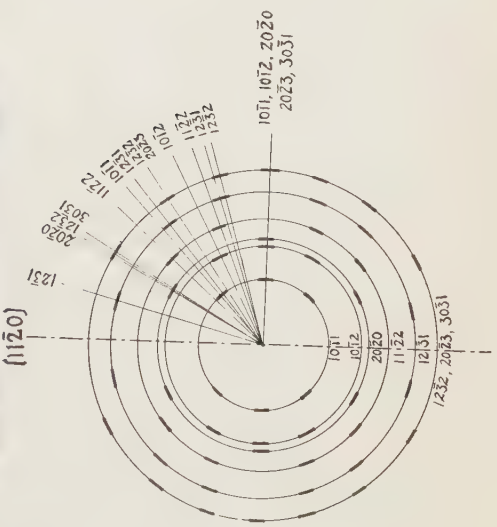


Fig. 3



A Study of the Minor Fluctuation of the Atmospheric Pressure (IV)

By Tadao Namekawa

(Received September 21, 1935)

Part III. Seiches of Lakes or Bays due to Microbaric Disturbances[1]

1. Introduction

Earthquakes are counted among the causes of seiches, but all observers agree that the majority of seiches are of meteorological origin. Prof. Chrystal and E. M. Wedderburn[2] enumerate 8 different causes for the development of seiches, the most important of which, they say, is microbaric disturbances, except in cases of shallow lakes. This paper, as part of the author's microbarographic study, is devoted to seiches due to microbaric disturbances, apart from a general discussion of the development of seiches. The microbarograms adopted and compared here are those recorded at Kyoto. The mareograms are those recorded in the Bay of Ôsaki, Wakayama Prefecture. They were taken under the direction of Dr. Nomitsu, Professor of Oceanography of our Geophysical Institute. In regard to the seiches of the bay, Mr. Y. Toyohara[3] has already published a report. His report, therefore, is to be referred to for general descriptions, etc. But, unfortunately, the bay is situated at some distance from Kyoto (Ca. 80 km.) And so, limnograms recorded in the Lake Biwa, which is a large lake lying east of Kyoto, are adopted in addition. Unfortunately again, complete limnograms can be obtained nowhere else except at Ôtsu, which is on the southern part of the lake, a part which must be considered an arm of the lake stretching far into the land. Therefore, the limnograms at Ôtsu belong to what Prof. Chrystal regards as exceptional cases, where the influence of wind is remarkable. Wind, indeed, is observed to have a striking influence on the

1. An outline of this part of the paper was read at the Annual Meeting of the Physico-Mathematical Society of Japan in Oct. 1931. 2. Trans. Roy. Soc. Edinb. **41**; Q. J. Roy. Met. Soc. **68** 211–217 (1922). 3. These Memoirs. A. **15** No. 3. (1932).

development of seiches in the southern part of the lake. Concerning the general causes of the development of seiches there, a paper will be made public by Mr. T. Takahashi, the authors collaborator in the present study, so that nothing will here be said about them. Although conditions were not very satisfactory, as has just been stated, for the comparison between microbarograms and limnograms, the author was able to get some fairly good examples, and he hopes that an examination of these examples may contribute something to the study of the phenomenon in question. For these reasons, the author has come to the decision to lay this paper before the public.

2. Examinations of the Mareograms at the Bay of Ôsaki

The dates of the development of seiches in the bay, their mean periods, the meteorological data at Wakayama and the results of microbarographic observations at Kyoto,—these since July, 1926, when a tide-gauge was first set up in the Bay of Ôsaki, up to May, 1930 are compared in Table I. It may be mentioned in this connection that Mr. Y. Taguchi has reported on the relation between the secondary undulations in the Bay of Shimotsu, which is adjacent to that of Ôsaki, and on the meteorological factors. In Table I, microbaric disturbances are proved to be the most important cause of the seiche-development, as Prof. Chrystal and others believe. In my discussion, henceforth, a line will be drawn between secondary undulations due to periodic fluctuations of pressure, i. e., atmospheric waves, and those due to sudden non-periodic disturbances.

Table I

Limnographic Osc.	Microbarographic Note	P.T.	Date	Wind and Press. at Wakayama		
				Direction	m/s	mm(700+)
			1926			
15^h29-9^h30 VII (8)	11^h29-10^h30 (6,27)	C	29a	WSW	2	51.8
18^h18-10^h19 VIII (9,19)	14^h-21^h18 (13)	C	18p	—	0	55.5
$3^h\ 3-12^h\ 4$ IX (19,7)		T	3a	N	2	57.0
0^h-23^h17 IX (9,19)	0^h-23^h17 (15,13)	T	17a	NNE	4	51.0
$0^h\ 7-15^h\ 8$ X (7,19)	$23^h\ 6-24^h\ 8$ (9,24)	B	7a	NE	3	64.0
16^h22-9^h23 XI (20,7)	18^h22-8^h23 (9)	C	22p	NE	3	64.2
$9^h\ 7-19^h\ 8$ XII (17,7)	$6^h\ 7-19^h\ 8^*$(7,9)	D	7a	ESE	2	59.8
3^h-24^h20 XII (17,8)	21^h19-10^h20 (6)	D	20a	NE	2	70.8

Limnographic Osc.	Microbarographic Note	P.T.	Date	Wind and Press. at Wakayama		
				Direction	m/s	mm(700+)
1927						
9^h -18^h 7 I (18,9)	6^h -21^h 7 (7)	C	7a	E	5	64.0
15^h24- 9^h25 II (21,28)	16^h24- 7^h25*	D	24p	—	0	67.0
15^h 8-19^h 9 III (19,6)	9^h -17^h 8 (8)	D	8p	S S E	7	64.9
15^h -24^h10 III (8)	(Squall at 22^h10^m)	C	10p	—	0	55.5
6^h12- 9^h14 III (9)	2^h13-22^h14 (10,20)	C	12a	—	0	66.1
0^h -12^h20 III (19)		C	20a	N N E	6	54.0
18^h23-20^h24 V (19,8)	15^h23-11^h24* (14,6)	D	23p	W S W	3	58.7
15^h -21^h 8 X (8)	15^h -17^h 8 (5)	D	8p	—	0	57.3
4^h 8-21^h 9 XII (21,8)		C	8p	E	4	65.2
1928						
0^h -12^h10 I (9,21)	1^h $-$ 8^h10* (11)	D	10a	S	3	66.2
0^h -24^h12 V (8)	14^h12- 6^h13 (16,5)	T	12a	—	0	49.6
0^h13-15^h14 VI (19,7)	13^h13-10^h14* (7,13)	C	13a	S E	4	53.0
18^h21-18^h22 VI (18,7)	8^h -14^h21 (12)	D	21p	W	2	54.2
0^h24- 9^h25 VI (9,19)	16^h24- 6^h25 (8)	C	24a	—	0	58.9
0^h -24^h25 IX (9)	6^h -12^h25 (7)	D	25a	—	0	57.5
0^h -15^h30 IX (21,9)	16^h29- 9^h30 (10)	B	30a	E N E	2	59.0
0^h -24^h 5 X (8,19)	14^h 4-22^h 5 (14)	B	5a	—	0	63.2
0^h18-24^h19 XI(19,11)	23^h17-24^h19 (7,11)	C	18a	E N E	2	68.5
1929						
3^h $-$ 8^h 7 IV (7,17)	7^h $-$ 9^h 7*	D	7a	S S E	5	51.8
21^h19- 6^h21 IV (9)	13^h20- 5^h21	C	19p	—	0	60.6
18^h26- 9^h27 IV (7)	19^h26- 4^h27* (13,4)	D	26p	S S W	10	53.9
4^h -16^h18 V (19)	0^h -14^h18 (9)	B	18a	E N E	3	58.6
15^h -21^h 9 IX (25)	16^h 9-11^h10 (32)	T	9p	N E	4	51.4
0^h21- 5^h22 IX (19,21)	14^h19- 7^h22*(38,15)	T	21a	—	1	59.9
6^h28- 6^h30 IX (19,9)	13^h28- 7^h30 (31)	T	28a	E N E	2	61.3
0^h $-$ 9^h 4 X (19,7)		T	4a	N E	2	60.8
15^h 6$-$ 6^h 9 XI (18,9)	19^h 5-24^h 9* (14,8)	D	6p	—	1	69.0
0^h10- 9^h11 XI (19,7)	16^h 9$-$ 7^h11 (12)	B	10a	E N E	3	68.1
0^h20-18^h21 XII (7)	10^h19-22^h21* (14)	C	20a	E N E	2	59.5
1930						
0^h26-15^h27 II (21,7)	12^h26-14^h28* (6,12)	C	26a	E N E	3	60.5
0^h -15^h 4 III (19)	6^h -20^h 4 (16)	D	4a	N N E	4	61.4
0^h -12^h 5 V (9)	17^h 4-11^h 5 (7)	B	5a	N N E	5	58.0

Remarks. The first column shows the Duration-Times of the occurrences of secondary undulations of Ôsaki Bay.

The figures denote the time and date, Roman numerals the month, and the figures in bracket the periods of predominant undulations. The second column shows the durations of the corresponding disturbances of the microbarogram at Kyoto.

* indicates a remarkable disturbance. The figures in brackets are the periods of the predominant waves of pressure. The third column shows the types of pressure-distribution on the weather charts, and the adopted notations are as follows:

B: when border of anticyclone passes near our observatory. C: when cyclones are near. D: when discontinuous lines pass near. T: when typhoon situates far south region or passes near.

The fourth column shows the time corresponding to the third and fifth columns. The figures denote the date; (a) and (p) indicate 6^h and 18^h respectively.

The fifth column shows wind and pressure at Wakayama Meteorological Observatory.

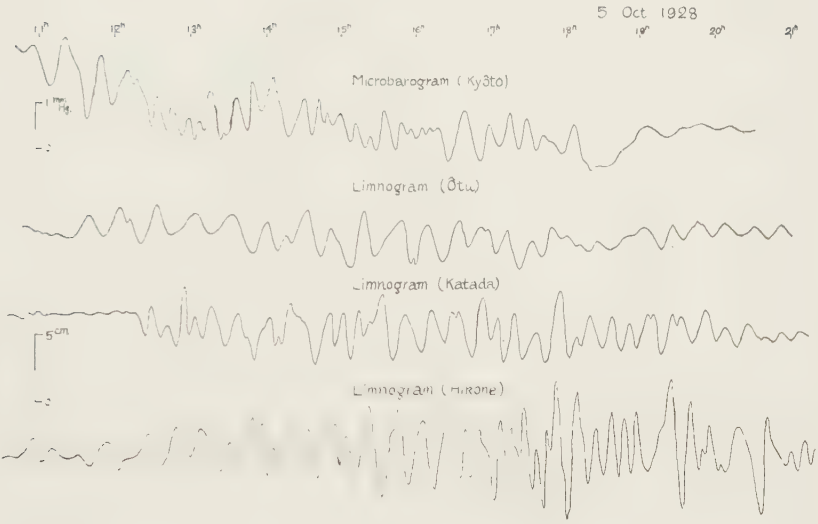
3. Seiches of Lakes or Bays due to Travelling Waves of Pressure

Although it is well known that periodic fluctuation of pressure is one of the important causes of the development of seiches, a good example is rarely found. A typical example, therefore, is given first of all.

Ex. Developed Seiches of Oct. 5th, 1928. The description of the microbaric disturbances of the day is given in the foregoing chapter treating the classification of disturbances types. Fig. 1 shows the microbarogram at Kyoto and the limnograms at Lake Biwa. Fig. 2 is a reproduction of mareograms at Ôsaki and Shimotsu. In these figures, the period of the waves of pressure is 7, 10, and 19 min., and the period of the seiches of Lake Biwa is 20–25 min. at Otsu; and 12, 21 min. at Katada; 7, 11, and 19 min. at Hikone; 19.0, 9.5, and 7.0 min. at Ôsaki; 19.0 and 7.0 min. at Shimotsu. Each of these observed periods is approximate to one of the theoretical periods and also to one of the periods of microbaric fluctuations. Moreover, on that day, the wind was almost calm and no trace of violent phenomena such as squalls was experienced in the vicinity of Japan, so that there is no other way of accounting for the seiche-development but by supposing that it depends on microbaric disturbances. The microbaric disturbance of the day, in view of both its great amplitude and of its long duration, is a very rare phenomenon. And from the fact that the seiches and secondary undulations are unusually remarkable in other places, it may safely be asserted that this is one of the best examples of its kind.

It is a well-known fact, as shown in this example, that the seiche-development is observed, when the period of fluctuations of pressure

Fig. 1



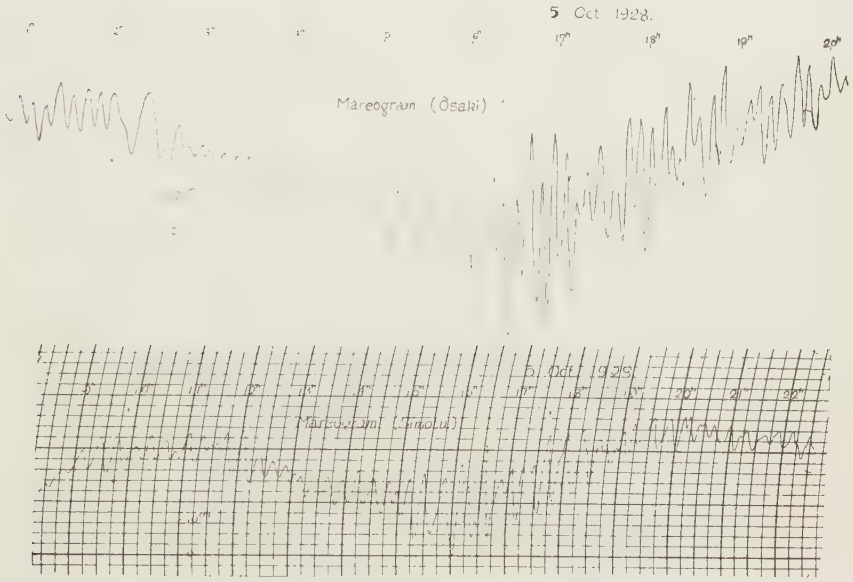


Fig. 2

coincides with that of the seiches. But fluctuations of pressure seem, hitherto, to have been considered to be stationary. The author had already noticed, as recorded in the foregoing part of this paper, that waves of pressure travel. Now, travelling waves of pressure can cause

resonance, which may simply be explained in the following way. In this discussion, the author neglects the turbulance of the sea or a lake, which, must actually modify the character of the seiches. But the essence of the author's argument is in no way altered by the omission. To make matters simpler, the forced wave of pressure is assumed:

$P_0 = P\cos k(x - Vt)$. (1) The equation of the motion of a long wave and the equation of the continuity are written down in the usual notation:—

$$\frac{\partial^2 \xi}{\partial t^2} = gh\frac{\partial^2 \xi}{\partial x^2} + \frac{kP}{\rho}\sin k(x - Vt), \quad (2) \qquad \eta = -h\frac{\partial \xi}{\partial x}. \quad (3)$$

(i) Solutions for a lake. The boundary conditions, in this case, are:— $\xi = 0$ at $x = \pm l$ where $2l$ stands for the length of the lake. A simple appropriate solution for this case is:—

$$\xi = -\frac{P}{k\rho c^2(m^2-1)}\left[\sin k(x - Vt) - \frac{1}{\sin 2klm}\cdot \left\{\sin k(l + Vt)\sin km(x - l) + \sin(l - Vt)\sin km(x + l)\right\}\right]. \quad (5)$$

$$\eta = \frac{hP}{\rho c^2(m^2-1)}\left[\cos k(x - Vt) - \frac{m}{\sin 2klm}\cdot \left\{\sin k(l + Vt)\cos km(x - l) + \sin k(l - Vt)\cos km(x + l)\right\}\right]. \quad (6)$$

where $m = V/c$ and $c = \sqrt{gh}$. This solution is obtained immediately by referring to the theory of the forced tide of canals.[1]

(ii) Solutions for a bay. The boundary conditions, in this case, are:— $\xi = 0$ at $x = l$, $\eta = $ *only forced wave i. e. free wave* $= 0$ *at* $x = 0$, where $x = 0$ shows the position of the entrance to the bay, and l shows the length of the bay. The solutions, in this case, are

$$\xi = -\frac{P}{k\rho c^2(m^2-1)}\left[\sin k(x - Vt) - \frac{\sin k(l - Vt)}{\sin 2klm}\cdot \left\{\sin km(x + l) - \sin km(x - l)\right\}\right]. \quad (7)$$

$$\eta = -\frac{hP}{\rho c^2(m^2-1)}\left[\cos k(x - Vt) - \frac{m\sin k(l - Vt)}{\sin 2klm}\cdot \left\{\cos km(x + l) - \cos km(x - l)\right\}\right]. \quad (8)$$

In (6) and (7), if $V = c$ and consequently $m = 1$, then $\eta \to \infty$ apparently,

1. Lamb, Hydrodynamics. 5 ed. 252.

but, on the contrary, η converges to a finite value in this case. But when $\sin 2klm \to 0$, $\eta \to \infty$ This corresponds to the cases of resonance. In other words, $2klm = s\pi$ (s : integer) (9). Now suppose that T_i is the calculated seiche-period of a lake or bay, namely,

$T_i = 2l/ic$ for a lake (10), $T_i = 4l/(2i-1)c$ for a bay (11), ($i = 1, 2, 3, \ldots\ldots$),

conditions in (9) prove to be, $T_i/T = s/2i$ for a lake (12), $T_i/T = s/2i-1$ for a bay (13). The foregoing is a treatment of a simple ideal case, but it leads to comprehension of the relations in more complicated cases.

4. Seiches due to Rapid Fluctuations of Barometric Pressure

Fig. 3

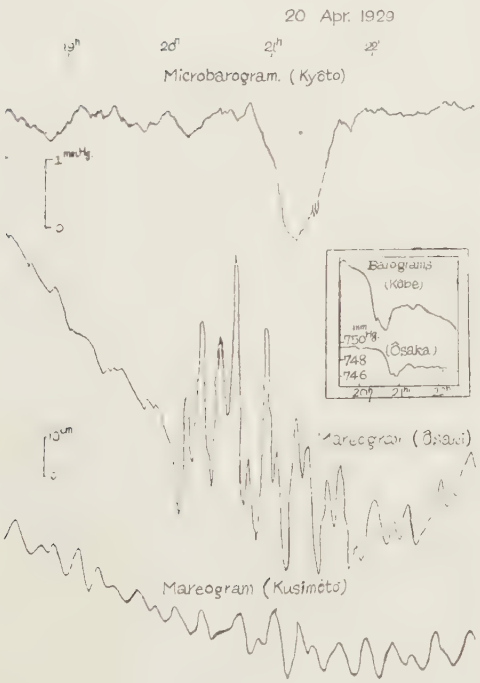
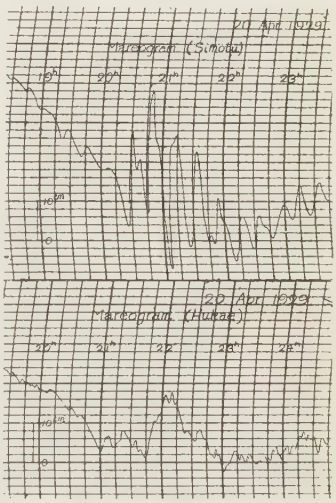


Fig. 4



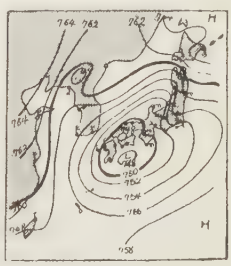
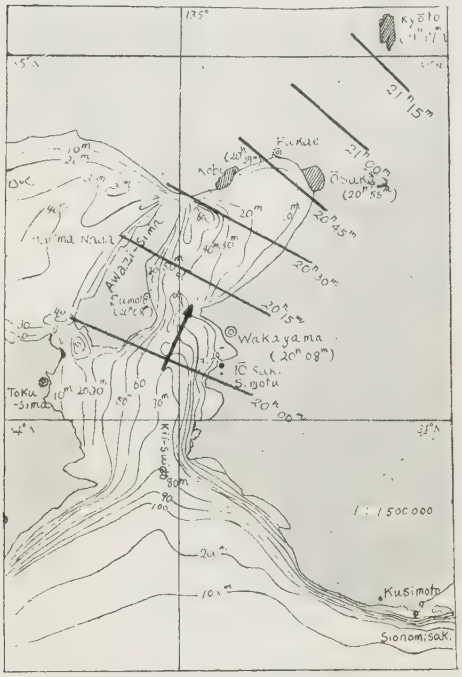


Fig. 5

Weather Chart.
18h, 20th, Apr. 1929.

Ex. 20th Apr. 1929. A well-developed seiche was recorded by the mareograph at about 20^h in the Bay of Ôsaki. (See Figs. 3 and 4) On the weather chart of the time (Fig. 5), a typhoon is seen in the northern part of the Pacific Ocean near the southern coast of Japan, but it is not directly attacking the bay. Pressure distributions of similar kind have several times been witnessed, but such a seiche has rarely been recorded. On the other hand, microbarograms at Kyoto show the passage of a microbarographic depression at about 21^h. The state of its propagation can be determined by the barograms of neighbouring observatories (Fig. 6). Thus it is inferred that the depression passed the Bay of Ôsaki at about 20^h, from which time the seiche developed in the bay. This striking coincidence necessarily leads to the assumption that the developed seiche was due to the passage of the microbarographic depression.

Fig. 6



But the physical explanation of this phenomenon is not simple. The depth of fluctuation of pressure being 4mm Hg. at most, its statical effect alone cannot account for a variation of water surface amounting to 5.4 cm. Reports of researches of this kind are very rare. So far as the author knows, Mr. Marmer[1] is the only investigator, who has given, in "The Tide," an example of this phenomenon illustrated by a diagram. Mr. Marmer says, in his report, that there were no peculiar features about the wind, only there was a kick in the barogram, in correspondence to which, a seiche occurred. Although he gives no further description nor discussion, his report has been a great help to the present author, who has endeavoured to complete the physical explanation of this problem, but has not as yet been successful. Below is stated the author's opinion, which may be somewhat speculative. According to Prof. J.

Proudman, an elevation of the water-surface, with a closed end at $x=0$, and with an infinite extension in the positive direction of x, generated by pressure-disturbance on a sea-surface of uniform depth, can be shown by the following equation[2];

$$\zeta=\frac{1}{1-V^2/c^2}\left\{F(t-x/V)-\frac{V}{c}F(t-x/c)\right\}$$

where $\xi=F(t-x/V)$ $c=\sqrt{gh}$.

Accordingly, at $x=0$, $\zeta=\frac{1}{1+V/c}F(t)$

and if $V/c\rightarrow-1$, $\zeta\rightarrow\infty$

which shows the occurrence of resonance. Actual cases are, of course, different from this simple, ideal case in various points. But, qualitatively considered, where a coast lies on one side, (where the depth (h) extends over a fairly large portion of the sea) and where the condition,

$$\frac{\textit{Velocity of propagation of barometric fluctuation}}{\textit{Velocity of free wave}}\fallingdotseq-1$$

is satisfied, it is reasonable to suppose that the fluctuation of the water surface at the coast may become several times as great as its statical value. Of course, this magnifying power depends on the length of the domain in which the condition is satisfied. Looking at the matter from another point of view, in the actual example just presented, the microbaric disturbance is propagating toward NNE at the rate of 25.5 m/s. If we assume $h=50$ m, 60 m and 70 m, then $c=22$, 24 and 26 m/s respectively. Therefore, the domain where $V/c\fallingdotseq-1$, must be a sea where $h=60$–70 m. This value cannot occur in the interior of the Bay of Ôsaki, but in the Kii Channel outside the bay, may occur over a considerable area. (See Fig. 6) From these facts, it is to be supposed that a fairly great rise and fall of the water-surface occurred outside the bay owing to the resonance effect which has just been described. C. K. M. Douglas[3] gave a similar example, when he treated a disturbance of the sea-surface occasioned by a thunderstorm occurring in the English Channel. After having simplified the records at the Bay of Ôsaki, and eliminated the seiche from them, there still remains the variation of the water-level. This variation is about five times as great as the statical value due to pressure. Magnifications of this degree can be regarded as possible by the application of the principle of resonance

1. Marmer "The Tide" 151 (1926). 2. M. N. R. A. Soc. Geophys. Suppl. **II 4** 197 (1929). 3. Met. Mag. **64** 187 (1929).

to this example. It is easily to be understood that, when there is a variation of the sea-level at the mouth of the bay, a secondary undulation develops in the interior. Now, at the mouth of the bay ($x=0$), if we put $\eta=f(t)$, the rise and fall of the sea-surface which it causes in the bay are shown by the equation :—

$$\eta=\frac{2c}{l}\sum_{s=0}^{\infty}\sin\frac{(2s+1)\pi x}{2l}\int_0^t F(\mu)\sin\sigma_s(t-\mu)d\mu.$$

Now, if $F(t)=a\sin nt$ for $0<t<t_1$ and $F(t)=0$ for $t>t_1$, then

$$\eta=\frac{2ca}{l}\sum_{s=0}^{\infty}\frac{1}{\sigma_s^2-n^2}\left[\sigma_s\sin nt-n\sin\sigma_s t\right]\sin\frac{(2s+1)\pi x}{2l} \qquad (0<t<t_1),$$

$$\eta=\frac{2ca}{l}\sum_{s=0}^{\infty}\frac{1}{\sigma_s^2-n^2}\left[n\sin\sigma_s(t-t_1)\cos nt_1+\sigma_s\cos\sigma_s(t-t_1)\sin nt_1 - n\sin\sigma_s t\right]\sin\frac{(2s+1)\pi x}{2l} \qquad (t>t_1),$$

and if $\sigma_m/n\to 1$ then $\eta_m=\frac{2ca}{l}\cdot\frac{\sin\sigma_m t-\sigma_m t\cos\sigma_m t}{2\sigma_m}\times\sin\frac{(2m+1)\pi x}{2l}$ $(0<t<t_1)$.

Therefore, when the period of forced vibration of the bay agrees with that of free vibration, the seiche develops to a remarkable extent. But in the example now under consideration, this effect is not great. To sum up; in this example, conditions in the outer sea being favourable for the variation of pressure causing resonance, a fairly great disturbance of the sea-surface occurs, which, in its turn, develops the seiche in the bay as a secondary phenomenon.

5. Remarks and Conclusion

(i) The reproduction of the records of 15^{h} 17th Sept. 1926, when a typhoon passing near the Bay of Ôsaki, caused a very great seiche to occur is given in Y. Toyohara's report. But in this case also, a microbarographic depression is observed to have accompanied the seiche. (See Fig. 7) Moreover, the beginning of the seiche synchronizes, not with the passage of the centre of the typhoon, but with the passage of the microbarographic depression. As this minor depression propagated NNE at the rate of 27 m/s, there was, as in the foregoing example, an area of greater or smaller extent near the mouth of the bay, where $V/c\fallingdotseq -1$.

Fig. 7.

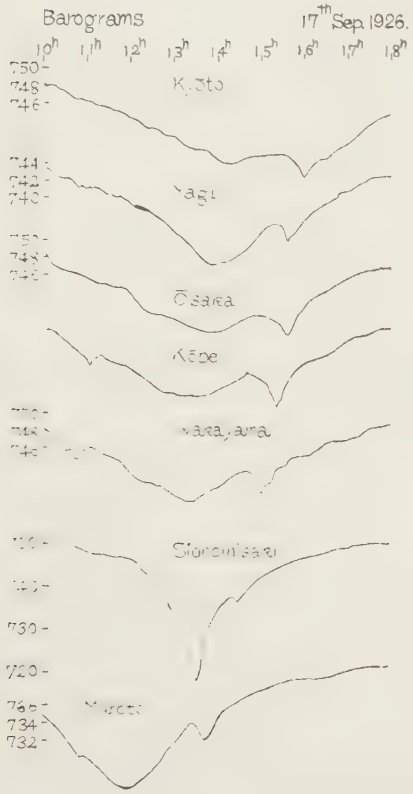
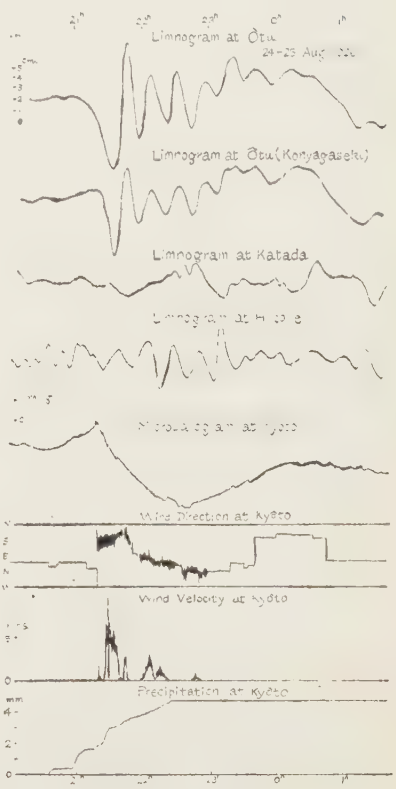


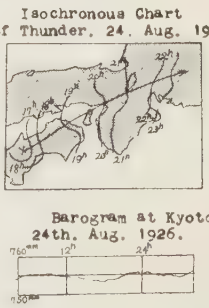
Fig. 8.



(ii) The microbaric disturbances with a propagating velocity of 60 m/s, described in § 1, Section V, Part II, are not accompanied by any remarkable seiche. The reason is perhaps that there is no domain near by where $V/c \fallingdotseq -1$.

(iii) Examples of seiches corresponding to squalls are not unfrequently met with in the southern portion of Lake Biwa (which must be regarded as a shallow bay). Fig. 8 shows one such example. In cases of squalls, pressure changes are always accompanied by wind changes. As this example occurred in shallow water, the variation of the wind must have been its chief cause, but a pressure variation must be of more importance in the development of seiches in a deep lake.

Fig. 8b.



Conclusion

(i) By comparing microbarograms and limnograms, the author came to the same conclusion as Prof. Chrystal, that the most important cause of seiches, except in shallow lakes, is microbaric disturbances.

(ii) By citing a typical example of seiches due to the periodic variation of pressure, and basing his argument on the fact that the variation is progressive, the author has modified somewhat the view hitherto taken of the matter.

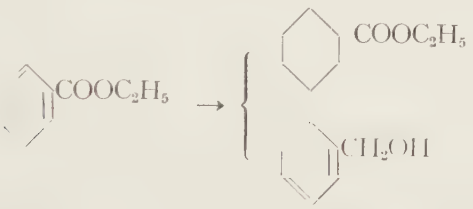
(iii) By applying J. Proudman's theory to a typical example of seiches occasioned by non-periodic but rapid variation of pressure, the author showed that when the area of the sea which satisfies the condition $V/c \fallingdotseq -1$ is extensive, in the proximity of the mouth of a bay, there is a remarkable development of the seiche.

Catalytic Reduction of Aromatic Carboxylic Acid Esters under High Pressure and Temperature

By **Keisaku Mitsui**

(Received September 25, 1935)

Prof. P. Sabatier succeeded in reducing ethyl benzoate into hexahydrobenzoate by applying a temperature of 180° and hydrogen in the presence of reduced nickel.[1] Using copper-chromium, copper-barium-chromium, or copper-calcium as catalyst, H. Adkins and K. Folkers,[2] however, obtained benzyl alcohol from ethyl benzoate. The same reaction had been obtained by Bowveault and G. Blanc,[3] who used ethyl alcohol or amyl alcohol[4] with sodium as reducing agent. Consequently aromatic carboxylic acid esters can be converted into their hexahydro-compounds or aromatic alcohols according to the catalysts employed.



Using reduced nickel, which was prepared from nickel nitrate converted into oxide by heat of about 350°, and reduced in the hydrogen stream at 290°−320°, the author endeavoured to reduce aromatic carboxylic acid esters under high pressure of hydrogen and at high temperature into hexahydro-compounds. The following is the report of the experiment.

(I) Ethyl benzoate (B.p.$=208°-212°$; $D_4^{25}=1.0441$; $n_D^{25}=1.5625$) was heated under 100 atmospheric pressures of hydrogen with 10 percent of reduced nickel. At 100°, hydrogen began to be absorbed and the reaction at 150° was remarkable and was completed with the absorption of 3 mols hydrogen by being kept at 150°−190° for 2 hours. 90 mol percent of the reaction product consisted of ethyl hexahydrobenzoate (B.p.$=190°-195°$; $D^{25}=0.9524$; $n_D^{25}=1.4396$) but neither benzyl alcohol nor benzoic acid was present. Repeating the reaction in

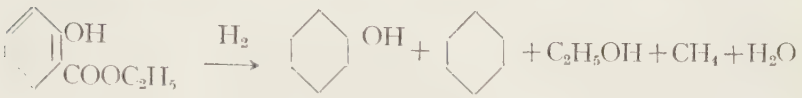
(1) P. Sabatier: Compt. rend., **154**, (1912), 925. (2) H. Adkins, K. Folkers: J. Amer. Chem. Soc., **53**, (1931), 1095, **54**, (1932), 1145. (3) L. Bowveault, G. Blanc: Bull. Soc. Chim., **31**, (1904), 666. (4) V. Markownikow: Ber., **25**, (1892), 3357.

ethyl alcohol solution, it was confirmed that the solvent has no effect on the yield and reaction velocity.

Subsequently, ethyl phenyl acetate (B.p.$=111^{\circ}/20$ m.m.; $D_4^{25}=1.0277$; $n_D^{25}=1.4949$) was reduced in hydrogen which began to be absorbed at about 150°, and after keeping the temperature $180^{\circ}-200^{\circ}$ for 15 hours, $2\frac{1}{2}$ mols hydrogen were absorbed. The reaction product consisted of 90 mol percent of ethyl cyclohexyl acetate. (B.p.$=100^{\circ}-102^{\circ}/20$ m.m.; $D_4^{25}=1.1255$; $n_D^{25}=1.5206$)

(II) From the fact that the reduction velocity of phenol was greater than that of benzene, it was supposed that the hydroxyl group might have some effect on the reduction velocity of catalysis. The writer therefore conducted an experiment with ethyl salicylate (B.p.$=132^{\circ}-133^{\circ}/35$ m.m.; $D_4^{25}=1.1255$; $n_D^{25}=1.5206$), which was heated under 100 atmospheric pressures of hydrogen, it being expected that the reaction would occur more easily than in the above cases. But even at 200° no reaction occurred, so the temperature was raised to 240° and hydrogen began to be absorbed, and by maintaining this temperature for 6 hours $4\frac{1}{2}$ mols hydrogen were absorbed. The reaction product consisted of 75 mol percent cyclohexanol, cyclohexane, and ethyl alcohol. This experiment indicated that salicylic acid ester was dissociated into phenol and carbo-ethyoxyl group. The former were transformed into cyclohexanol and cyclohexane under high pressure of hydrogen and temperature.

In the next experiment, ethyl esters of meta- and para-hydroxybenzoic acid were reduced under high pressure and temperature by aid of the catalyst. From para-hydroxybenzoate (M.p $=112^{\circ}$), after 2 mols of hydrogen had been absorbed at about 200°, 40 mol percent of para-hydroxyhexahydrobenzoate (B.p.$=252^{\circ}-258^{\circ}$; $D_4^{25}=1.1664$; $n_D^{25}=1.4694$) were obtained. But from the meta-isomer (M.p.$=72^{\circ}$; B.p.$=187^{\circ}-188^{\circ}/31$ m.m.) 3 mols of hydrogen being absorbed at 200°, 75 mol percent of meta-hydroxyhexahydrobenzoate (B.p.$=156^{\circ}-160^{\circ}/33$ m.m.; $D_4^{25}=1.0678$; $n_D^{25}=1.4683$) were obtained. In the reaction of meta- and para-isomers as it differes greatly from that of the ortho-compound, no liberation of the carboxyl group occurred.



From the above mentioned experiments with ethyl benzoate, ethyl phenyl acetate and ethyl hydroxybenzoate, it is concluded that esters of aromatic carboxylic acid are converted into hexahydrocompounds by reducing at 200° under 100 atmospheric pressures of hydrogen in the presence of reduced nickel; benzene nucleus is hydrogenated by the activated hydrogen, and the reaction is altogether different from that in which copper-chromium is used as catalyst, since it chiefly activates the carboxyl group.

Experiment

(I) Catalytic Reduction of Ethyl Benzoate[1]

30 gms. of this ethylbenzoate of the physical constants B.p.$=208°-212°/753$ m.m.; $D_4^{25}=1.0441$; $n_D^{25}=1.5025$ were electrically heated in an autoclave, under 100 atmospheric pressures of hydrogen at 26° and with 10 percent of reduced nickel. The depression of the pressure in the autoclave began at 90° and became rapid at 140°, the reaction being completed in 3 hours with absorption of 3.3 mols hydrogen (Fig. 1). The reaction product ($D_4^{25}=0.953$; $n_D^{25}=1.439$) was examined, 30 gms. of liquid being fractionated with the following results:—

Fraction	B.p.	Yield	D_4^{25}	n_D^{25}	M.R.	Ester-value
1	185°–190°	7.0%	0.9506	1.4374	—	—
2	190°–195°	84.7	0.9524	1.4396	43.12	364
3	195°	7.0	—	—	—	—

Fraction, B.p. 190°–195°, was colourless liquid found to consist of ethyl hexahydrobenzoate by being converted into hexahydrobenzoic acid (M.p.$=30°$) by hydrolysis. From the physical constants of the fractions; B.p.$=185°-190°$ and 190°–upwards, the reaction product was assumed to consist principally of ethyl hexahydrobenzoate. Thus ethyl benzoate was reduced into ethyl hexahydrobenzoate with a yield of 90 percent. Catalytic reduction of ethyl benzoate was tried in the ethyl alcohol solution. The conditions and the experimental result are shown in the following table and Fig. 2.

1 S. Komatsu, K. Mitsui: The Mem. of the Sci. K. I. U. A. 14 (1931), 297.

Sample	Ethyl alcohol	Initial press.	Temp.	Time	Absorption of hydrogen
50 g.	50 g.	97 atm./28°	180°–220°	$2\frac{1}{2}$ hrs.	3.3 mols

Fig. 1.

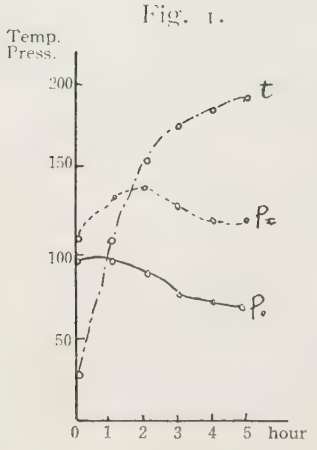
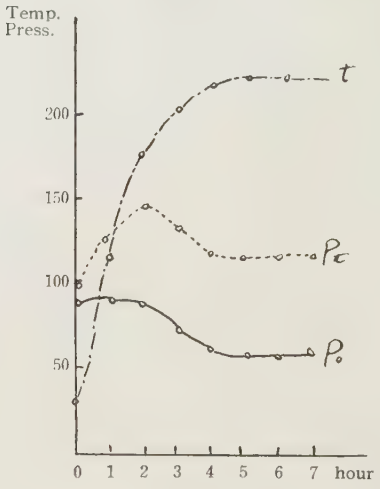


Fig. 2.



After the reaction was completed, the solvent was expelled by distillation and the physical properties of the residue (50 gms.) were measured: $D_4^{25}=0.930$; $n_D^{25}=1.432$

The physical constants and yield of ethyl hexahydrobenzoate purified by fractional distillation were:—

B.p.	Yield	D_4^{25}	n_D^{25}	M.R.	Ester-value
190°–196°	88%	0.9531	1.4411	43.22	366

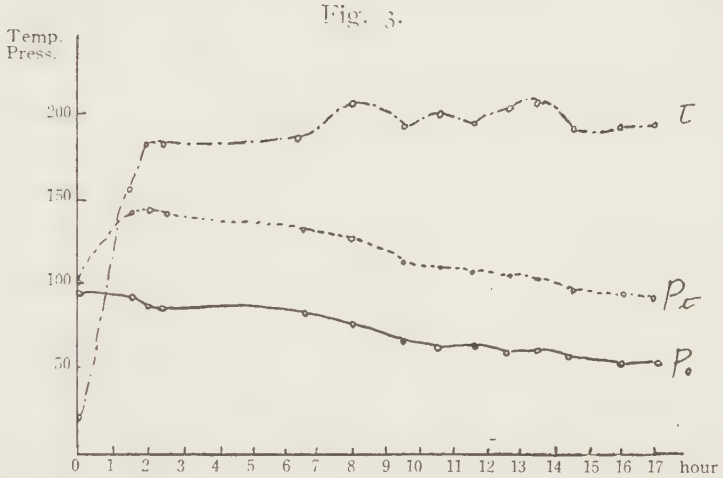
(II) Catalytic Reduction of Ethyl Phenyl Acetate

Ethyl phenyl acetate (B.p.=111°/20 m.m.; $D_4^{25}=1.0277$; $n_D^{25}=1.4949$) was reduced in the presence of 10 percent of reduced nickel under the following conditions.

Sample	Initial press.	Reaction temp.	Time	Absorption of hydrogen
25 g.	100 atm./20°	180°–200°	17 hrs.	2 mols

Absorption of hydrogen began at 140° and became rapid at 150°, as will be seen from Fig. 3, and 2 mols of hydrogen were absorbed in 17 hrs.

Fig. 3.



The reaction product was a weak acidic yellowish liquid and the yield was 23 gms. and the physical constants were: $D_4^{25}=0.924$ $n_D^{25}=1.446$.

After the reaction product was neutralized with caustic alkali and dried, 20 gms. of the neutral part, separated from the acidic part, were fractionated under reduced pressure and the physical properties of the fractions obtained:

Fraction	B.p.	Yield	D_4^{25}	n_D^{25}	M.R.	Ester-value
1	90°–100°/20m.m.	6.5%	0.9321	1.4455	—	300
2	100°–102°/20m.m.	75.0	0.9415	1.4456	48.0	315
3	residues and loss	14.0	—	—	—	—

The second fraction was assumed from its physical constants to be ethyl cyclohexyl acetate, and was confirmed to be so by combustion analysis.

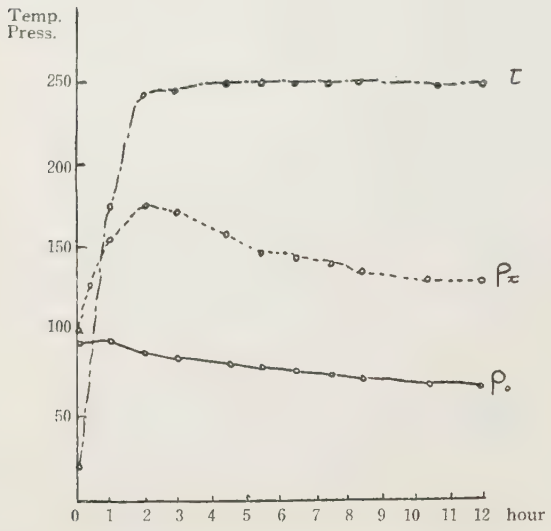
Sample	CO_2	H_2O	C%	H%
0.1145 g.	0.2994 g.	0.1070 g.	71.1	10.4
	Calc. for $C_{10}H_{18}O_2$		70.6	10.6

The first fraction, as will be seen by the constant, contained some ethyl cyclohexyl acetate and the third fraction consisted of ethyl phenyl acetate.

(III) (a) Catalytic Reduction of Ethyl Salicylate

31 gms. of ethyl ortho-hydroxybenzoate (ethyl salicylate) (B.p.= 132°–133°/35 m.m.; $D_4^{25}=1.1255$; $n_D^{25}=1.5216$) were reduced under the

Fig. 4.



similar conditions with the former cases and the reduction began at 160° and became rapid at 200°. (cf. Fig. 4.) During about 10 hours heating at 250°, $4\frac{1}{2}$ mols hydrogen were absorbed. 28 gms. of reaction product of constants $D_4^{25}=0.916$; $n_D^{25}=1.426$ were separated by fractional distillation into 6 gms. of ethyl salicylate (B.p.= 230°−232°; $D_4^{25}=1.1220$; $n_D^{25}=1.5200$; ester value 308), an other fraction of 22.0 gms. The latter was again fractionated :—

Fraction	B.p.	Yield	D_4^{25}	n_D^{25}	M.R.
1	75°– 85°	5.7%	0.7784	1.4248	27.58
2	85°– 95°	20.0	0.8596	1.3658	—
3	95°–160°	6.7	—	—	—
4	160°–165°	42.0	0.9407	1.4605	29.16
5	residues & loss	4.3	—	—	—

The first fraction was confirmed to be cyclohexan by analysis after it had been distilled with sodium.

Sample	CO_2	H_2O	C%	H%
0.1430 g.	0.4497 g.	0.1841 g.	86.6	14.3
	Calc. for C_6H_{12}		85.7	14.3

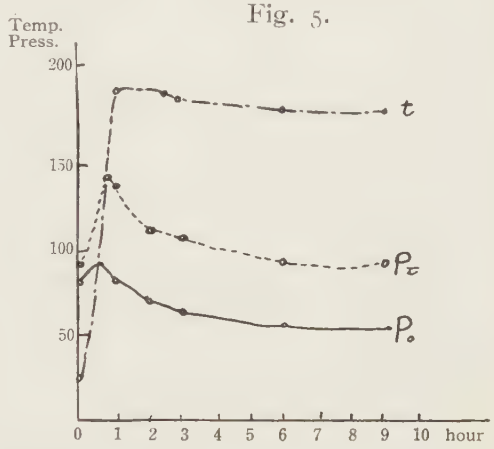
The second fraction was distilled again and was ascertained to be ethyl alcohol from the iodform reaction and formation of acetic acid ester. The 4th fraction which showed the physical constants of cyclohexanol, was confirmed to be so by measurement of its melting point (79°) after changing it into phenylurethane, and by analysis after purifying it.

Sample	CO_2	H_2O	C%	H%
0.2471 g.	0.6467 g.	0.2600 g.	71.4	11.7
	Calc. for $C_6H_{12}O$		72.0	12.0

(b) Catalytic Reduction of Meta-Hydroxybenzoate

20 gms. of ethyl meta-hydroxybenzoate (M.p.=72°; B.p.=187°–188°/31 m.m.) were dissolved in 20 gms. of absolute ethyl alcohol, and the mixture was reduced with 10 percent of reduced nickel under the following conditions similar to the case of ethyl salicylate. As will be seen in Fig. 5, some of hydrogen was absorbed at 140° and most of it while the temperature was raised from 150° to 180°, and 3 mols of hydrogen were absorbed in 5 hours. 18 gms. of reaction product of physical properties $D_4^{25}=1.049$; $n_D^{25}=1.470$ were obtained. By fractional distillation 17.8 gms. of the higher fraction were separated from the lower fraction of ethyl meta-hydroxybenzoate and were fractionated again into fractions with the following physical properties.

Fig. 5.



Sample	Initial press.	Temp.	Time	Absorption
20 g.	92 atm./23°	170°–190°	5 hrs.	3.0 mols

Fraction	B.p.	Yield	D_4^{25}	n_D^{25}	M.R.	Ester value
1	135°–156°/33m.m.	5.8%	1.0055	1.4647	—	220.8
2	156°–160°/33m.m.	82.0	1.0678	1.4683	44.8	310.6
3	residues & loss	9.3	—	—	—	—

The first fraction was found to be meta-hydroxyhexahydrobenzoate containing some of other lower boiling part. From its physical properties and ester value, the second fraction seemed to be meta-hydroxyhexahydrobenzoate, which was confirmed by elementary analysis.

Sample	CO_2	H_2O	C%	H%
0.4106 g.	0.9371 g.	0.3478 g.	62.2	9.4
	Calc. for $C_9H_{16}O_3$		62.8	9.3

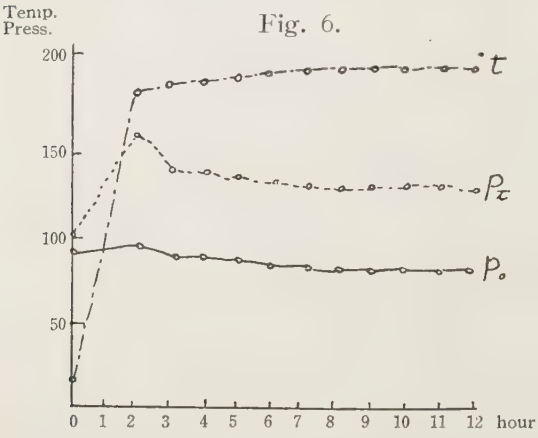
(c) Ethyl Para-Hydroxybenzoate

The ester of the constants M.p.=112°; Ester value=332 was

reduced with the same amount of absolute ethyl alcohol under the following conditions:

Sample	Initial press.	Temp.	Time	Absorption
20 g.	100 atm./17°	180°–200°	8 hrs.	2.0 mols

Fig. 6.



The absorption of hydrogen began suddenly at 180° and 2 mols of hydrogen was absorbed in 9 hours. (cf. Fig. 6) The product was separated into ethyl para-hydroxybenzoate. 18.0 gms. of the fraction (B.p.=255°–258°; D_4^{25}=1.065; n_D^{25}=1.468), were fractionated into fractions with the following results:—

Fractions	B.p.	Yield	D_4^{25}	n_D^{25}	M.R.	Ester value
1	–252°	4.7%	1.0593	1.4784	—	—
2	252°–258°	40.0	1.0664	1.4694	44.9	322
3	residues & loss	1.4	—	—		

The second fraction was confirmed to be ethyl para-hydroxyhexahydrobenzoate by its physical properties and chemical elementary analysis.

Sample	CO_2	H_2O	C%	H%
0.2011 g.	0.4625 g.	0.1625 g.	63.0	9.0
	Calc. for $C_9H_{16}O_3$		62.8	9.3

The first fraction contained, as will be seen from the physical constants, a small amount of the same substance as the second fraction. Ethyl hydroxybenzoate (9.1 gms.) was confirmed by converting it into para-hydroxybenzoic acid (white crystal, M.p.=210°) by hydrolysis.

In conclusion, the author wishes to express his sincere gratitude to Prof. Dr. S. Komatsu for his kind guidance and encouragement throughout this work.

August 1932
Laboratory of Organic and Bio-Chemistry,
Kyoto Imperial University.

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